

SPECTROSCOPY OF DISORDERED MATERIALS







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ABSTRACT

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Mixed crystals of $(KBr)_{1-x}(KCN)_x$ show a complicated structural behavior at low temperatures which includes an intriguing orientational glass state. Better understanding of these relatively simple disordered systems may improve our understanding of the glassy state in general.

We have used the Brillouin spectroscopy to measure the acoustic phonon properties in the KBr-KCN alloys. All aspects of the spectra, such as Brillouin shift, linewidth and intensity, were found to qualitatively agree with Michel's microscopic theory. From the frequency and the width of the acoustic phonon, we determined the reorientation rate of CN^- quadrupoles as a function of temperature, which can be described by an Arrhenius law.

Quasi-elastic light scattering in $(KBr)_{1-x}(KCN)_x$ was measured using a high resolution tandem Fabry-Perot interferometer. The width of the quasi-elastic peak was found to have a strong temperature dependence. We suggest that this peak is dynamic in origin and is related to the reorientation of the cyanide dipolés.

We observed the appearance of symmetry forbidden scattering peaks in the Brillouin spectra of $(KBr)_{1-x}(KCN)_{x}$ in the presence of a uniaxial stress. This effect can be

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explained as a stress-induced birefringence altering the polarization state of the scattering light. There are no observable changes in Brillouin shift and width induced by such a stress.

The dielectric loss and capacitance of an x=0.5 sample was determined using a high precision bridge. Only one loss peak appears at ~30 K in the temperature interval from 1.2 K to 294 K, which indicates that there is no coupling between quadrupole and dipole moments at around quadrupolar freezing temperature (~80 K).

A calorimetric technique was used to investigate thermal properties of $(KBr)_{0.5}(KCN)_{0.5}$ at T<1 K. The specific heat of the sample is in good agreement with reported values. Samples which have undergone different thermal treatments show different heat drift behavior. Analysis of the time-decay of temperature after application of a heat pulse reveals that the decay curve follows a stretched exponential form.

Finally, the acoustic sound wave in propylene glycol was studied using a Brillouin scattering technique. The relaxation rates obtained in the gigahertz frequency range were compared with the low frequency specific heat data in terms of the Vogel-Tamman-Fulcher law and the scaling law. The latter was predicted by recent hydrodynamic theories for the glass transition.

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CHAPTER 1

Introduction

For an amorphous solid the essential aspect in which its structure differs from that of crystalline solid is the absence of long-range order. Some typical disordered systems are shown in Fig. 1.1: (c) amorphous silicon (positional disorder), (E) liquid crystals (orientational order but positional disorder), (d) polymers (both orientational and positional disorder). Despite tremendous theoretical and experimental efforts, understanding the properties of amorphous solids is far behind understanding those of crystals. This is because one can no longer use powerful tools such as Brillouin zones, Bloch states, etc., which accompany periodicity in the crystals (for a review, see Ref. 1).

Recently an unusual type of disordered system, $(KBr)_{1-X}(KCN)_X$, has attracted a great deal of attention. Upon cooling the mixed crystal with CN⁻ concentration 0.01 < x < 0.6 will freeze into an orientational glass state in which CN⁻ axes are randomly orientated as shown in Fig. 1.1(b). More detailed structure can be seen in Fig. 1.2 (after Ref. 2). • As this state is derived from a crystalline parent phase, the experimental and theoretical

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Fig. 1.1 Schematic comparison of ordered and disordered materials: (a) KBr Crystals, (b) . (KBr)_{1-x}(KCN)_x mixed crystals, (c) amorphous silicon, (d) polymers, (e) liquid crystals.





(KBr)_{I-x}(KCN)_x

Fig. 1.2 Crystal structure of cubic $(KBr)_{1-x}(KCN)_x$ (after Ref. 2).

description should be easier than that of conventional glasses. It is hoped that studying this system may contribute to a better understanding of glasses in general. For this reason $(\text{KBr})_{1-x}(\text{KCN})_x$ systems were cited by Physics Today as one of the five most interesting new topics in condensed matter physics in 1985.³ There are several excellent review articles on this subject.^{2,4-6}

Fig. 1.3 shows the phase diagram of $(\text{KBr})_{1-x}(\text{KCN})_x^6$ which reveals three main regions: (1) paraelastic or cubic high temperature phase, (2) the ferroelastic non-cubic state for $x>x_c(~0.57)$ and $T<T_c(x)$, (3) an orientational glass state for $x<x_c$ and $T<T_f(x)$. This phase diagram is analogous to that of dilute magnetic systems where the three regions are referred to as paramagnetic, ferromagnetic and spin glass respectively.⁷

At high temperatures, one finds a NaCl-like cubic structure for all CN⁻ concentrations where CN⁻ ions perform fast reorientation. At 168 K pure KCN undergoes a first order phase transition into an orthorhombic structure with CN⁻ elastic quadrupoles aligning along <110> directions. As the temperature reaches 83 K, KCN will become antiferroelectrically ordered due to the CN, NC degeneracy being lifted by the electric dipole interaction.

The ferroelastic phase transition temperature T_c will decrease on substituting Br⁻ ions in the KCN lattice until a critical CN⁻ concentration x_c ^{-0.57} is reached.

Fig. 1.3 The phase diagram of $(KBr)_{1-x}(KCN)_x$ (after Ref. 6). T_f^Q and T_f^D are the quadrupolar and dipolar glass freezing temperatures respectively; both are dependent on the probe frequency and the CN⁻ concentration.



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Below x_c , no structural phase transitions have been observed. The freezing temperature T_f can be determined by different techniques such as dielectric and neutron scattering. For x<0.01 CN⁻ ions are considered as isolated rotors in the KBr crystal field and glassy behavior disappears. The present thesis concentrates on the properties of mixed crystals with 0.01<x<0.57.

 $(KBr)_{1-x}(KCN)_{x}$ is disordered in two ways. Firstly the CN⁻ and Br⁻ ions are randomly distributed over the anion sublattice (referred to as the compositional disorder). Secondly the CN⁻ ions are disordered with respect to their orientations in the cubic lattice (referred to as orientational disorder). Since the compositional disorder in $(KBr)_{1-x}(KCN)_{x}$ is less important than the orientational disorder,² we will only consider the orientational glassy behaviors in this mixed system.

A wide variety of experimental techniques have been used to investigate $(KBr)_{1-x}(KCN)_x$. These include: inelastic neutron scattering,^{8,9} Brillouin light scattering,¹⁰⁻¹² ultrasonic,¹³⁻¹⁶ dielectric,¹⁷⁻¹⁹ low temperature thermal properties,^{2,20-24} X-ray,²⁵⁻²⁶ neutron diffraction,²⁷ pendulum,^{28,29} and NMR³⁰ measurements.

The main experimental facts may be briefly summarized as six important features: (1) The freezing temperature T_{f} depends on the frequency of the probe. As the probe frequency increase, T_{f} shifts to higher

temperature. This indicates that the glass phase transition in $(KBr)_{1-x}(KCN)_{y}$ is a relaxation phenomenon rather than a static one. (2) Due to the weak dipole moment of the CN^{-} ion (0.3 D) the dipolar relaxation is only a secondary process following the primary relaxation process which is characterized by a cooperative freezing of the quadrupolar degrees of freedom. (3) The onset of the orientational glass state is signaled by anomalies in the temperature dependence of the quadrupolar susceptibilities. The most direct evidence is that the elastic constant C_{44} exhibits a minimum at T_f . (4) The dielectric loss peak in $(KBr)_{1-x}(KCN)_{x}$, is very broad and indicates that there is a wide distribution of CN relaxation times. (5) $(KBr)_{1-v}(KCN)_{v}$ exhibits the low temperature (<1 K) thermal properties of amorphous solids. Its specific heat is roughly linear in temperature (T) and is logarithmically dependent on measuring time, and the thermal conductivity is proportional to T^2 . (6) The orientational glassy state may consist of very fine ferroelastic microdomains.

Theoretical efforts are being undertaken to describe these glassy behaviors in $(\text{KBr})_{1-x}(\text{KCN})_x$.³¹⁻³⁹ The first theoretical approach showing that strain defects in alkali halides can produce a glassy low temperature state has been outlined by Fischer and Klein.³¹ Recently more detailed models have been proposed by Sethna et al.^{37,38} and by Michel,³⁹ Sethna's et al. theory mainly focus on the

cyanide dipolar relaxation and low temperature thermal properties. This theory has quantitatively shown that the time-dependent specific heat and the dielectric loss peak can be understood in terms of 180° CN⁻ dipole reorientation from a tunneling or thermally activated motion through hindering barriers. Such barriers are produced by a mean field of elastic CN⁻-CN⁻ interaction. Michel's theory is much more fundamental and aims at the quadrupolar freezing process. Starting from a full Hamiltonian which includes the translation-rotation interaction energy and the random strain field - rotation coupling energy, this theory is able to explain glass state and the anomalous acoustic properties and central mode behavior in $(KBr)_{1-x}(KCN)_x$.

In the present work, we have systematically investigated the glass properties in $(\text{KBr})_{1-x}(\text{KCN})_x$. The Brillouin light scattering technique was used to study the acoustic phonon anomalies at the orientational glass transition in these mixed systems. The Brillouin spectra obtained with a high resolution Fabry-Perot interferrometer have been analysed using Michel's theory. We have also examined the quasielastic scattering in $(\text{KBr})_{1-x}(\text{KCN})_x$ and, in particular, determined the width of the quasielastic peak as a function of temperature around T_f . Dielectric measurements were performed in order to identify whether or not there is a quadrupolar relaxation contribution to the dielectric loss. We also measured the specific heat of

 $(KBr)_{0.5}(KCN)_{0.5}$ using a dilution refrigerator, focussing our attention on the low temperature relaxation behavior in the X=0.5 sample. In addition, we studied relaxation property in propylene glycol which exhibits a real glass "phase" transition upon cooling, using Brillouin spectroscopy. Short accounts of this work have appeared or will appear in scientific publications.^{12,40-44}

This thesis is divided into eight Chapters. Chapters 2 and 3 present results of Brillouin scattering^{12,40} and quasi-elastic scattering^{41,42} in (KBr) (KCN), respectively. Detailed experimental techniques are described and results are analysed with Michel's theory. Chapter 4 presents spectra of Brillouin scattering in (KBr) $_{1-x}$ (KCN)_x under a uniaxial stress.⁴³ In Chapter 5 we will report dielectric and light scattering measurements which were performed in an attempt to detect double relaxation processes in $(KBr)_{1-x}(KCN)_x$. In Chapter 6 the specific heat data at T<1 K in (KBr)_{0.5}(KCN)_{0.5} are presented. We will also discuss the low temperature relaxation behavior in the sample by analysing the heat drift data and temperature-time profile. Chapter 7 deals with relaxation property of propylene glycol studied by Brillouin spectroscopy.44 Finally in Chapter 8 results are summarized and future experiments are suggested.

CHAPTER 2

⁻ Brillouin Scattering Study of (KBr) $_{1-x}$ (KCN) $_{x}$

2.1 Background theory

The quantized vibrational mode in crystals is called a phonon in analogy with the photon of the electromagnetic wave. As a laser beam strikes a crystal, there will be interactions between photons and phonons resulting in light scattering.

The kinematics of the scattering process follow directly from the conservation of energy and momentum

between the incident (i) and scattered (s) photons and the phonons (q).⁴⁵ The positive sign is for an anti-Stokes event corresponding to a phonon annihilation while the negative sign is for a Stokes event corresponding to a phonon emission. Since $|\vec{k}_1| = |\vec{k}_3| = n\omega_1/c$ where n is the refractive index, and $|\vec{q}| = \omega_q/v_q$ where v_q is the velocity of the phonon, the conservation laws can be solved for the Brillouin shift⁴⁵

$$\omega_{\mathbf{q}} = \omega_{\mathbf{s}} - \omega_{\mathbf{i}} = \pm 2 \frac{V_{\mathbf{q}} \omega_{\mathbf{i}} n}{\mathbf{b}^{c}} \sin \frac{\theta}{2} \qquad (2.3)$$

where θ is the scattering angle and c is the speed of light. Classically this relation is called the Brillouin equation, and is identical to Bragg reflection from a grating of spacing $2\pi/q$ moving with velocity v_{σ} .

.Since the photon wave vectors (of order of 10⁵ cm⁻¹) are small compared with the Brillouin zone dimensions (of order of 10^8 cm^{-1}), information is provided only about phonons near $\vec{q}=0$. The process is usually referred to as Brillouin scattering, when the phonon emitted or absorbed is acoustic, and Raman scattering, when the phonon is We will focus our attention on the acoustic optical. phonons of the crystal as studied by the Brillouin scattering technique. Complementary to Brillouin scattering, acoustic properties may be studied by ultrasonic (US) and neutron scattering (NS) techniques. The former detects sound velocity; and attenuation in the MHz frequency range, while the latter provides phonon dispersion curves throughout the whole Brillouin zone with the acoustic phonon energy in the THz range.

Brillouin scattering, along with US and NS, has been used extensively to study the acoustic phonons in the mixed alkali halide - alkali cyanides crystals. A striking acoustic anomaly $^{46-48,13}$ was first found in the pure KCN

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crystals, which undergo a first order phase transition from a CN⁻ random oriented state to an ordered ferroelastic state at 168 K. The transverse acoustic phonon with T_{2g} symmetry, and the elastic shear constant associated with this phonon ($C_{44} = \rho v_q^2$) soften dramatically as the phase transition temperature is approached from above.

The soft mode behavior may be explained by a translational (phonon) and rotational (CN⁻) coupling mechanism.^{47,48,13} Such T-R coupling gives rise a strong lattice mediated CN⁻-CN⁻ interaction which favors CN⁻ orientational ordering, and results in a ferroelastic phase transition on cooling the KCN. The elastic constant (C₄₄) as a function of temperature (T) was well fitted by a mean field theory in terms of the Curie-Weiss-law,¹³

$$\frac{1}{C_{44}} - \frac{1}{C_{42}} = \frac{B}{T - T_0}$$
 (2.4)

where T_0 is the critical temperature at which C_{44} extrapolates to zero, C_{44}^{0} is the bare elastic constant and B is the T-R coupling constant. These fitting parameters have been tabulated in Ref. 13.

Brillouin scattering has also revealed softening of the phonon frequency $^{49-51}$ and broadening of the linewidth 51 for KCl doped with small amounts (~6 x 10^{19} cm^{-3}) of CN⁻ ions. These effects are significant only at very low temperature (<20K), where the upper tunneling level thermal

population, is small, thus permitting resonant scattering of phonons by those levels. Following Walton^{52,53} the shift $(\widetilde{\Delta \omega})$ of the phonon frequency due to such interaction may be expressed as

$$\frac{\Delta\omega}{\omega_{0}} = \sum_{i} \rho_{D} \left(\frac{A_{i}}{\omega_{i}} \right) \left(\frac{\omega^{2}}{\omega_{i}^{2}} - 1 \right)^{-1} \left(\frac{1 - \exp(-\beta\omega_{i})}{1 + \sum_{i} g_{i} \exp(-\beta\omega_{i})} \right)$$
(2.5)

where $\rho_{\rm D}$ is the defect density, $A_{\rm i}$ is phonon-defect coupling constant, $\omega_{\rm i}$ is the frequency of the tunneling level which has degeneracy $g_{\rm i}$, and $\omega_{\rm o}$ is the pure crystal phonon frequency. The interaction among CN⁻ ions has been neglected due to a very low CN⁻ concentration. By fitting eqn. (2.5) to experimental data, the coupling constant⁴ was determined for a KC1:CN sample.⁵⁰

In the mixed crystals $(\text{KBr})_{1-x}(\text{KCN})_x$ with 0.01<x<0.6, no structural phase transition occurs. Upon cooling from room temperature, the mixed crystals form an orientational glass state at a freezing temperature T_f which depends on CN⁻ concentration. The Brillouin scattering¹⁰⁻¹² and US¹³⁻¹⁵ and NS⁸⁻⁹ all show that the frequency of T_{2g} symmetry phonon dips to a minimum at T_f . This minimum moves to higher temperature with higher probe frequency: T_f ~70K for US, ~80K for Brillouin scattering, and ~90K for NS. ϵ It is apparent that the freezing is not a static phenomenon but a relaxational one. Depending upon

the probe's frequency, the CN^- may or may not appear frozen. When CN^- ions cannot respond to the probe any more, the system is referred to as frozen.

Michel and Rowe have developed a microscopic theory³² which can explain the minimum in the phonon frequency at T_f but fails to yield a corresponding maximum in the phonon attenuation.¹² On the other hand, the Curie-Weiss law was found to demonstrate softening of the T_{2g} mode at higher temperatures but deviated from experimental data near and below T_f .¹⁴ Recently Michel³⁹ has revised his theory. The new theory proposes that long range CN⁻ quadrupolar order is destroyed due to random strain fields induced by the difference in ionic radii between Br⁻ and CN⁻. Thus it has been suggested that the orientational glass state of the mixed system can be understood in terms of two competing effects: the lattice mediated CN⁻-CN⁻ coupling and the random strain fields-CN⁻ coupling.

In the present work, we have measured frequency, Finewidth and intensity of the T_{2g} acoustic phonon as a function of temperature using Brillouin scattering. The experimental results were found to be in good agreement with the latest version of Michel's theory.

Combining the data of the phonon frequency and damping, we obtained the CN[°] quadrupolar relaxation rate and the activation energy for CN⁻ quadrupolar reorientation in the pretransition region. The measurement of the

intensity of the Brillouin component has resulted in a determination of the photoelastic constant for mixed crystals.

2.2 Experimental

The optical arrangement of the experimental apparatus is shown in Fig. 2.1. An Argon ion laser (Innova Model 90-3, Coherent Co.) provided the exciting radiation at 5145 Å. A single frequency beam with a very narrow linewidth (<4MHz) was obtained by installing a temperature controlled solid etalon (Model 923, Coherent Co.) in the laser cavity. The aperture wheel located on the front of the laser head was adjusted to obtain a stable TEM₀₀ single mode. After a 30 minute warm up period, the laser was operated at typically 200 mw with an intensity stability ranging $\pm 0.5\%$.

The incident beam was focused in the sample by lens $L_1(f=20 \text{ cm})$. The scattered light was collected and collimated by lens (f=15 cm). A spatial filter, consisting of $L_3(f=15 \text{ cm})$, a pinhole $P_1(r=50 \mu \text{m})$, and lens $L_4(f=10.5 \text{ cm})$, screened out stray light in front of the interferometer. Here all lenses were plano-convex shaped. For minimum spherical aberration, the plane side of a lens faced the image.

Care must be taken in choosing the diameter, ϕ , of



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 P_1 : if ϕ is too big the spectral line will be anomalously broad; on the other hand, if ϕ is too small the spectral intensity will be reduced. A theoretical discussion of the spatial filter can be found in Ref. 54.

The light transmitted by the interferometer was focussed by a lens $L_5(f=30 \text{ cm})$, then passed through a filter F, and entered a photomultiplier (PMT). F is an interference filter with a very narrow transmission band of 10 Å centered at 5145 Å, and effectively baffles the inelastically scattered light arising from fluorescence and Raman (optical phonon) scattering from the sample. The PMT (Model R943, Hamamatsu Co.) has a low dark current 0.2x10⁻⁹ A at a gain of ~10⁶. A chamber (Model TE-104, Products for Research Inc.) provided thermoelectric cooling for the PMT tube resulting in a noticeable reduction of dark current compared with no-cooling operation. The interferometer and PMT are enclosed in a light-tight box which helps to reduce stray light, keeps the optics free of dust and minimizes the temperature variation in the enclosure.

The output of the PMT was processed by a photon counting electronic system which included a preamplifier and a discriminator (Model 511, MTN). The signal was digitized with an A/D converter and its values stored in the memory of a computer (IBM Compatible XT). The same computer, in conjunction with D/A electronics, provided the ramp voltage used in piezoelectrically scanning the Fabry-

Perot (FP) interferometer. The timing pattern used for the ramp was also used to address, sequentially, 1024 channels of the computer memory, so that the channel number was directly proportional to the frequency shifts passed by the FP. Hence spectral data were accumulated in the form of photon counts versus frequency of the scattered light.

The heart of the experimental system is the tandem multi-pass Fabry-Perot interferometer designed by $\int_{-\infty}^{\infty}$ Sandercock.⁵⁵ A single FP etalon consists of two highly reflecting parallel mirrors. The inner faces of the mirrors are optically flat to $\lambda/200$ before being overlayed with multi-layer dielectric coatings. The transmitted intensity (I^(t)) for normal incidence to an etalon is given by the Airy formula⁴⁵

$$I^{(t)} = I^{(i)} (1 - \frac{A}{1-R})^{2} \left(\frac{1}{1 + \frac{4R}{(1-R)^{2}}} \frac{\sin \frac{2\delta}{2}}{2} \right)$$
(2.6)

where $I^{(1)}$ is the incident light intensity, A is the absorption coefficient of the mirror, R is the reflectivity and δ is a phase angle between successive reflections. Light with a wavelength λ will be transmitted if a constructive interference condition is satisfied: $d=m\lambda/2$, where m is the order of interference and d is the distance between the two mirrors. The frequency separation between two neighboring maximum transmissions is called the free spectral range (FSR), and is given by FSR=c/2d, where c is

the velocity of light. The full width at half maximum (FWHM) of the transmitted light $(\Delta \nu)$ determines the resolution of the interferometer, and the finesse F is then defined as F=FSR/ $\Delta \nu$. The finesse is governed by several factors, such as mirror reflectivity, which will be discussed in the next chapter.

The contrast (C) of the fringe is the ratio of maximum to minimum transmission given by 45

$$C = \left(\frac{1 + R}{1 - R}\right)^2 \qquad (2.7)$$

For R ~90%, C is of the order of a hundred. This contrast is not sufficient for measuring in situations where the elastically scattered component of the scattered light exceeds the intensity of the Brillouin component by more than a factor of 10^5 .

The contrast can be increased by passing a beam through this tandem FP n times. The total contrast is then equal to $(2C)^n$. For n=2 it is three orders of magnitude greater than that of a single FP. Such an arrangement is referred to as a tandem multipass Fabry-Perot interferometer (TMFPI).

Besides increasing the contrast of the spectrum, TMFPI also serves to effectively increase the free spectral range by an order of magnitude resulting in the elimination of overlapping orders. In addition the resolution will be improved.

For Sandercock's system, the scanning mirrors of two interferometers are mounted on the same scanning stage with an offset angle α . The spacing of the two Fabry-Perot interferometers satisfies $d_2=d_1 \cos \alpha$. The first FP of spacing d_1 transmits the light at $\lambda_1=2d_1/m_1$, while the second FP of spacing d_2 at $\lambda_2=2d_2/m_2$. Only if $\lambda_1=\lambda_2$ will light be transmitted through the tandem combination. Therefore the FSR of the TMFPI is increased by a factor of 20 over that of single FP for an offset angle $\alpha=18^{\circ}$.⁵⁵

The scanning and alignment of TMFPI was controlled by a computer. Details will be given in the next chapter.

The single crystals were grown at the Crystal Growth Laboratory of the University of Utah from zonerefined KBr and KCN. The CN⁻ concentrations were confirmed by chemical analysis with an error of 3%. Samples were cleaved along (100) planes with a razor blade and typically had dimensions of 0.5 cm x 0.5 cm x 0.5 cm.

The sample was mounted in a conventional optical cryostat (Sulfrian Cryogenics Inc.) and cooled by conduction from liquid N_2 or He baths. To attain temperatures around 60-77 K, pumped liquid nitrogen was used. For temperatures in the range 120-294 K, a home made nitrogen-gas-flow cryostat was employed. A heater is wound on the sample mount to maintain a steady temperature. Temperatures were measured by a silicon diode at T<20 K and

by a Copper-Constantan thermocouple for T>20 K.

In order to measure the spectra of T_{2g} phonons which propagate along [110]-direction and are polarized in [001]-direction, a 90° scattering geometry was used. The (100) and (010) surfaces of the sample were perpendicular to the incident and the scattered light respectively.

The focussed beam must be located near the centre of the sample to prevent strong surface scattering. By adjusting the cryostat position, the light transmission through the crystal could be maximized, minimizing the surface reflections.

The linewidths were determined by fitting the Brillouin peak using the convolution of a Lorentzian function with the elastic peak which was used as an instrumental function. Considering the variation of the instrumental finesse and fitting errors, the linewidth measurements were accurate to within ±15 MHz.

2.3 Results and discussions

2.3.1 Frequency and width of the Brillouin peak

The frequency and full width at half maximum (FWHM) of the transverse acoustic phonon with T_{2g} symmetry for the x=0.5 sample are shown in Fig. 2.2 as a function of temperature. Interesting features in the figure are the


Fig. 2.2 Brillouin shift (*) and full width at half maximum (0) of the transverse phonon with T_{2g} symmetry for x=0.50 are plotted against temperature. Solid lines are guides for the eye.



Fig. 2.3 The temperature dependence of the Brillouin shift (*) and FWHM (0) of the T_{2g} phonon for x=0.35.

occurrence of a minimum in phonon frequency and a maximum in phonon linewidth. The temperature at which the minimum phonon frequency occurs is conventionally defined as the CN^- quadrupolar freezing temperature, T_f . The phonon width reaches a maximum at T slightly below T_f , and changes more dramatically than the phonon frequency around T_f . Similar behavior was also found in the x=0.35 sample as shown in Fig. 2.3. Comparing Fig. 2.2 and Fig. 2.3 we can see that T_f shifts toward lower temperature as the CN^- ion concentration decreases. T_f is about 80 K for x=0.5 and 70 K for x=0.35 a

The experimental results can be explained in the framework of the microscopic theory developed by Michel.³⁹ In this theory, the mixed alkali halide-alkali cyanide systems are described by a full Hamiltonian given by

 $H = K^{T} + V^{T} + K^{R} + V^{R} + V^{TR} + V^{SR}$ (2.8)

where the first two terms represent the pure translational (or acoustic displacement) energy. The third term is the kinetic energy of CN^- ions rotating. V^R describes a rigid octahedral potential which the CN^- ion experiences in the cubic lattice environment. V^{TR} accounts for the coupling between the acoustic translational modes and the $CN^$ reorientational modes, referred to as the T-R coupling. The last term represented the interaction of the orientational degrees of freedom of CN^- ions with the

random strain fields induced by the substitution of ellipsoidal CN⁻ ions by spherical Br⁻ ions. We will refer to this interaction as S-R coupling in short.

Starting from the above microscopic model, Michel has formulated dynamic response functions which are proportional to the differential scattering cross section for both the inelastic neutron scattering and the Brillouin scattering. The response function of the acoustic phonon mode with $T_{2\alpha}$ symmetry is explicitly given by³⁹

$$\phi = \frac{-\Delta_{11}(\vec{k})f(\omega)}{[\omega^2 - D_{11}(\vec{k},\omega)]^2 + [\omega\Delta_{11}(\vec{k})f(\omega)]^2}$$
(2.9)

$$f(\omega) = \frac{\lambda}{\omega^2 + \lambda^2}$$
(2.10)

and .

$$D_{11}(\vec{k},\omega) = M_{11}(\vec{k}) - \Delta_{11}(\vec{k})f(\omega)$$
 (2.11)

where $\langle \lambda \rangle$ is the CN⁻ reorientational relaxation frequency, $M_{11}(\vec{k})$ is the bare phonon frequency, $D_{11}(\vec{k},\omega)$ is the renormalized phonon frequency and variables ω and \vec{k} represent frequency and wavevector respectively. A rather complicated mathematical expression for $\Delta_{11}(\vec{k})$ can be found in Ref. 39, which basically describes an effective interaction among CN⁻ ions mediated by both the random field and the T-R coupling. From the denominator of eqn. (2.9), the linewidth which is associated with the attenuation of the phonon wave is given by

$$\Gamma = \omega \Delta_{11}(\vec{k}) f(\omega) \qquad (\vec{k} - 12)$$

Both the renormalized phonon frequency $(D_{11}(\vec{k},\omega)/M_{11}(\vec{k}))$ and the phonon linewidth (Γ) for $(KBr)_{0.6}(KCN)_{0.4}$ were calculated as a function of temperature by Michel. They are shown in Fig. (2.4) as a solid line and a dashed one respectively.

Comparing Fig. 2.2 with Fig. 2.4, we can see that there are some differences between the theoretical prediction and experimental data. Firstly the experimental linewidth Γ versus T around T $_{f}$ is much $_{\Im}$ sharper than the theoretical linewidth. Secondly Fig. 2.4 only presents calculated results for (KBr)_{0.6}(KCN)_{0.4}. For x=0.5, theoretical phonon frequency becomes zero and linewidth diverges when approaching the freezing temperature from above. Michel has attributed such unrealistic outcomes into the uncertainties in values of the microscopic interaction potential V^{TR} in eqn. (2.8).³⁹ Fox x<0.5 although there is some discrepancy, the general features of the theoretical curves are in reasonable agreement with the experimental results. The anomalous acoustic properties of $(KBr)_{1-x}(KCN)_{x}$ which are hidden in the complex mathematics of Michel's model can thus be explained as follows.

In pure KCN, there is a strong T-R coupling, resulting in a softening of the phonon frequency. Such T-R

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coupling also mediates an indirect interaction among CN ions which favors an orientational ordered state, and drives the cubic crystal undergoing a phase transition into a ferroelastic state upon cooling. Substituting Br ions for CN ions the KCN lattice produces two effects: firstly it leads to a reduction of the ferroelastic phase transition temperature via a decrease of the T-R coupling while at the same time it generates a random strain field due to the slightly different size between Br ions and CN ions. This random strain field will couple with the orientational degrees of freedom of CN ions (S-R coupling) and will tend to destroy the alignment of the CN ions. Therefore there is a delicate balance between the T-R coupling and the S-R coupling. The winner of this competition determines the low temperature phase. For CN concentration <0.57, the S-R coupling becomes dominant upon cooling, and suppresses the ferroelastic structural phase transivion, and causes the freezing into an orientational glass state. Hence the phonon frequency does not soften completely to zero. Instead it recovers from the minimum as temperature is further lowered from T_f. Since the inverse of Brillouin linewidth is proportional to the phonon lifetime, the maximum linewidth results as the T-R coupling reaches a maximum around T_f.

2.3.2 Quadrupolar relaxation in KBr:KCN

In contrast to a bromine ion, an aspherical shaped cyanide ion has both an elastic quadrupole and an electric dipole. With decreasing temperature, mixed crystals $(KBr)_{1-x}(KCN)_x$ with 0.01 < x < 0.6 will freeze into an orientational glass state. Volkmann et al.²⁸ classified two distinguishable relaxation mechanisms in KBr:KCN in terms of quadrupolar and dipolar processes. The freezing in of dipoles and quadrupoles occurs at different temperatures.

The dipolar process has been studied by dielectric measurements. 17719 A wide distribution of dipolar relaxation times and barrier heights has been revealed. The average reorientation rate of the CN⁻ dipoles was found to follow an Arrhenius law.

The quadrupolar process has been investigated using techniques⁸⁻¹⁵ which probe the elastic response of the solids. A plot of the probe frequencies against the inverse of the quadrupole freezing temperature T_f for $(KBr)_{1-x}(KCN)_x$ is found in Ref. 28, and also shows an Arrhenius behavior. However, there are only three data points for x=0.5 taken from neutron scattering⁸, Brillouin scattering¹⁰, and torsion pendulum^{28,29} experiments; thus, the value of the activation energy (8000 K) is uncertain.

frequency can provide valuable information about quadrupolar relaxation. Unfortunately, for 0.25 < x < 0.6, there is a heavy damping of the transverse sound waves in a considerably wide temperature range near T_f , resulting in a loss of the echoes.^{14,15} In Brillouin scattering experiments the loss is revealed in the temperature dependent broadening of the phonon width.

By analysing the frequency and linewidth of the T_{2g} symmetry phonon, which are shown in Fig. 2.2 and Fig. 2.3 of section 2.3.1 for x=0.5 and x=0.35, respectively, we have determined the CN⁻ quadrupolar relaxation rate as a function of temperature. Here we focus our attention on the temperature range about T_f and will refer to this range as the paraelastic regime.

The phonon frequency (ν) can be converted to sound velocity v using the Brillouin scattering equation

$$r = \frac{\nu \lambda_0}{2n \sin \theta/2}$$

(2.13)

where λ_0 (5145 Å) is the incident laser wave length, n is ,the index of refraction and θ (90°) is the scattering angle. In turn, the elastic constant C_{44} is related to the velocity of the transverse sound wave in the sample with density ρ by

$$C_{44} = \rho v^2$$
 (2.14)

Following Michel's theory, the CN orientational

modes are strongly coupled to the T_{2g} phonon mode. This bilinear translational and rotational interaction results in softening of the elastic constant in the paraelastic region. The dynamic effect on the elastic constant may be simply expressed ^{56,57} as

$$C_{44} = C_{44}(\infty) - \frac{\Delta C_{44}}{1 + i\omega\tau}$$
 (2.15)

where $C_{44}(\infty)$ is the elastic constant far from the coupling regime, ΔC_{44} represents the temperature dependence of the coupling, ω is the angular phonon frequency, and τ is the CN⁻ reorientation time. This equation can be separated into a real elastic part, measured by the Brillouin phonon shift in accordance with eqn. (2.14), and an imaginary part, which determines the phonon linewidth (Γ).

ReC =
$$C_{\infty} - \frac{\Delta C_{44}}{(1 + \omega^2 \tau^2)}$$
 (2.16)

$$\Gamma - \Gamma_{\infty} = \frac{q}{2\pi\rho v} ImC = \frac{\tau \Delta C_{44}}{(1 + \omega^2 \tau^2)} \frac{q^2}{2\pi\rho}$$
 (2.17)

where q is the wavevector, Γ is the phonon width and Γ_{∞} represents additional sound attenuation not due to quadrupole-phonon coupling.

For a complete analysis of the effect of coupling on the acoustic mode behaviour, the microscopic model of

the interaction between the acoustic mode and CN⁻ ions is required. The detailed coupling mechanism has been discussed in Michel's theory, and in the last section. Combining eqns. (2.14), (2.16) and (2.17) the relaxation time is expressed as

$$\tau = \frac{\Gamma(T) - \Gamma_{\infty}}{[v_{\infty}^2 - v^2(T)]} \cdot \frac{2\pi}{q^2}$$
(2.18)

Here we use the room temperature value for v_{∞} . The linewidth measured in the temperature interval 120K<T<300 K is nearly T-independent and is taken as Γ_{∞} , which is probably due to the attenuation from static defects. We have ignored the contribution to the phonon linewidth due to the anharmonic effect which is only significant at very high temperature (>300 K).

The logarithm of the inverse relaxation time $1/\tau$ versus 1/T has been calculated via equation (2.18) for x=0.35 and x=0.5. The results are shown in Fig. 2.5. The necessary parameters are listed in Table 2.1. The index of refraction for the mixed crystals is a linear interpolation between KBr (n=1.559) and KCN (1.410). The solid lines in Fig. 2.5 are best fits of an Arrhenius relation.

$$1/\tau = 1/\tau_0 \exp[-E_0/k_pT]$$
 (2.19)

where τ_0 is the time between two consecutive attempts for a CN⁻ quadrupole to cross the energy barrier E_0 , and k_B is



Fig. 2.5 The log of the inverse quadrupolar relaxation time against 1/T. The symbol * represents x=0.5 data, 0 for x=0.35 data. Solid lines are best fits. The data from neutron scattering (+) and previous Brillouin scattering (•) are also plotted for comparison.

the Boltzmann's constant. The values of E_0 and $1/\tau_0$ obtained from fitting are also included in Table 2.1

The value of the attempt frequency is too high to be consistent with a single ion process. It can be understood in a qualitative fashion if two CN⁻ ions are involved: the activation energy involved is close to twice the barrier height for a single ion. The decrease in activation energy for x=0.35 could then be due to a larger contribution from single ion relaxation. We have in fact been able to fit the data for x=0.35 using a sum of two exponentials with activation energies of ~600 K and ~1200 K.

Considering the substantial difference between the present result, E_0 ~1000 K, and the previous one, E_0 ~8000 K, for x=0.5, we have re-examined all previous data and presented them in Table 2.2. The relaxation time τ_f at the freezing temperature T_f is defined by $2\pi\nu_f\tau_f^{=1}$ where ν_f is the phonon frequency or resonance pendulum frequency at T_f . The values of ν_f and T_f for the previous Brillouin experiment¹⁰ are smooth interpolations of data between x=0.34 and x=0.56. As is evident from Fig. 2.5, the data from neutron and previous Brillouin scattering¹⁰ are in very good agreement with our present Arrhenius relation. However the data from the torsion pendulum experiment²⁹ is substantially different from the solid line in Fig. 2.5. This may be due to a dramatic change in probe frequency:

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Summary of the parameters used in analyzing the elastic quadrupolar relaxation.

X(mole%)	$\Gamma_{\infty}(MHz)$	v _∞ (m∕s)	n	$\nu_0(Hz)$	E _O (K)
0.35	68	1139	1.507	5.3 x 10 ¹⁵	849
0.5	72	1070	1.485	1.3×10^{17}	1230

Table 2.2

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Summary of the data at quadrupolar freezing temperature for x=0.5.

Experiment	T _f (K)	1000/T _f	$\nu_{f}(Hz)$	$1/\tau_{f}(Hz)$
Neutron Scatt. ⁸	100	10.0	9.7x10 ¹⁰	6.1x10 ¹¹
Brillouin Scatt. ¹⁰	. 78	12.8	2 x10 ⁹	1.3x10 ¹⁰
Pendulum ²⁹	75	13.3	1 x10 ²	6.3x10 ²

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the propagation of sound in solids is an adiabatic process for frequencies greater than a megahertz, while the pendulum resonance is an isothermal process due to its very low frequency (10^2 Hz). It is not valid to directly compare the adiabatic and isothermal relaxation times.⁵⁸

In conclusion, the CN quadrupolar reorientation rate was found to follow an Arrhenius law. The data from neutron and previous Brillouin scattering are in very good agreement with the present results. If one includes the pendulum experimental datum, this Arrhenius relation will break down. Further torsion pendulum experiments measuring shear elastic constants as a function of frequency may clarify this difficulty.

2.3.3 Intensity of the Brillouin component

When a light beam passes through a dielectric medium, the incident electric field induces oscillation dipoles along its path. In a macroscopic approach, the individual atomic dipole moments combine to form a macroscopic polarization vector. The scattered light is thus radiated by the oscillatory macroscopic polarization, which is subject to the Maxwell equation.

The polarization (\vec{P}) induced by the incident field (\vec{E}_i) in the absence of any excitations of the scattering volume is given by⁴⁵

 $\vec{P}(\vec{r},t) = \epsilon_0 \, \overset{\circ}{\chi}_0 \vec{E}_1(\vec{r},t) \qquad (2.20)$

where ϵ_0 is the permittivity of vacuum and $\ddot{\chi}_0$ is the first-order susceptibility of the medium. The effect of excitations in the medium is to modulate the susceptibility. To a first order approximation, the change in susceptibility is linearly proportional to the excitation amplitude X(\vec{r} ,t). Therefore eqn. (2.20) can be rewritten as⁴⁵

$$\vec{P} = \epsilon_0 (\vec{\chi}_0 \vec{E}_1 + \vec{\chi} X \vec{E}_1)$$
 (2.21)

where χ is the second-order susceptibility that describes the modulation. The first term of eqn. (2.21) represents oscillation at the same frequency as the incident field and contributes only to elastic scattering, while the second term of the polarization describes radiation of the inelastic contribution to the scattered light. The inelastic scattering differential cross section is further given by⁴⁵

$$\frac{d\sigma}{d\Omega} \propto \langle |\hat{e}_{s} \hat{X} X(\vec{k}, \omega) |\hat{e}_{i}|^{2} \rangle$$
(2.22)

where $X(\vec{k},\omega)$ are the Fourier components of $X(\vec{r},t)$, \hat{e}_i and \hat{e}_s are incident and scattered light polarization unit vectors respectively. The bracket <...> denotes an average over the thermal probability distribution.

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In Brillouin light scattering, long wavelength acoustic phonons produce elastic deformation in a crystal, which in turn gives rise to the variation of the susceptibility. It is called the photoelastic effect. The excitation amplitudes are the atomic displacements from the equilibrium lattice points. The differential cross section for the Brillouin component can be explicitly expressed as⁴⁵.

$$I = \frac{d\sigma}{d\Omega} = \frac{k_B T \omega_0^2 V}{32\pi^2 c_0^4 \rho v^2} |\vec{e}_s \cdot \vec{p} \cdot \vec{e}_i|^2 \qquad (2.23)$$

where c is the speed of light, ρ the crystal density; ω_0 is the incident light frequency, \vec{P} is the photoelastic (the Pockel's) matrix, v is the velocity of the acoustic wave, T is temperature and V is the scattering volume.

Combining both eqn. (2.23) and the Brillouin eqn. (2.3) which relates the phonon frequency (ν) to the velocity (v), we obtain

$$I = \frac{d\sigma}{d\Omega} = N \frac{T}{\nu^2}$$
(2.24)

where N is a temperature independent constant. Therefore the scattering intensity is primarily functions of temperature (T) and phonon frequency (ν).

The intensity of the acoustic phonon with T_{2g} symmetry was measured as a function of temperature in

 $(KBr)_{0.5}(KCN)_{0.5}$ as shown in Fig. 2.6 by stars. The value of each data point was obtained by integrating the Brillouin component over a fixed frequency range and normalizing to the integrated intensity taken at room temperature. The major source of error was either the statistical fluctuation in the photon counts or the variation in the Fabry-Perot interferometer alignment. From Fig. 2.6 it is evident that the Brillouin intensity increased as the crystal was cooled down until T_f was reached; this intensity decreased upon further cooling.

Substituting $\nu = 4.7$ GHz, I=1 at room temperature (295 K) for the x=0.5 sample into eqn. (2.24), we obtain N=0.0749. Using the phonon frequency in Fig. 2.2 and corresponding temperature, we have calculated the Brillouin intensity with eqn. (2.24). The results are shown in Fig.. 2.6 by the open circles, and are in good agreement with the experimental data.

As discussed above, the Brillouin intensity is essentially determined by the modulated susceptibility. For $(KBr)_{1-x}(KCN)_x$ systems, this susceptibility can be calculated based on Michel's microscopic model.³⁹ Specifically the susceptibility (χ) with T_{2g} symmetry is given by

$$x = \frac{x^0}{1 - x^0 \delta}$$
 (2)

(2.25)



Fig. 2.6 Integrated Brillouin peak counts for the T_{2g} symmetry phonon as a function of temperature for x=0.5 normalized to the integrated peak count at room temperature are indicated by stars. The open circles represent the calculated values of the differential cross-section equation.

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where

$$\chi^{0} = \frac{xy}{T} (1^{\circ} - x(1-x)) \frac{sh^{2}}{T^{2}}$$
 (2.26)

where x is the CN⁻ concentration, y and s describe the expectation values of the CN⁻ orientational variables, h is the strength of the random strain field, T is temperature and δ represents the translation-rotation coupling. The calculated curve of χ versus T is shown in Fig. 2.7 for various CN⁻ concentrations after Michel.³⁹ For x=0.5, the theoretical χ diverges at T_f and is in disagreement with our experimental data as shown in Fig. 2.6. Michel considered that the discrepancy is due to some uncertainty in the microscopic interaction potentials.³⁹ If we neglect the x=0.5 curve in Fig. 2.7, the general features in the theoretical curves in Fig. 2.7 are quite similar to the experimental results in Fig. 2.6.

In $(\text{KBr})_{1-x}(\text{KCN})_x$ systems, the formation of an orientational glass state is clearly marked by a maximum in susceptibility at T_f as demonstrated in Fig. 2.6 and 2.7. Similar behavior can also be found in the spin glass systems. A typical example is the Au:Fe system⁵⁹ where the iron solute atoms carry a magnetic moment and occupy sites randomly in the gold lattice. The interaction among neighboring moments results in the freezing in of magnetic spins upon cooling. At T below T_f the spins have no longrange magnetic order, but instead are found to have static



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Fig. 2.8 Magnetic susceptibility $\chi_{M}(T)$ for two Au:Fe spin glass alloys. The full line represents the zero field limit (after Ref. 59).

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orientations which vary randomly over macroscopic distances. Fig. 2.8 shows the magnetic susceptibility⁵⁹ of Au:Fe alloys for different Fe concentrations. A cusp-like peak is clearly seen in these curves. The maximum in the susceptibility shifts to higher temperature with increasing Fe concentration. Comparing Fig. 2.6-2.7 for KBr:KCN and Fig. 2.8 for Au:Fe, the analogy between the elastic quadrupolar glass and the magnetic/spin glass is striking.

During the course of this experiment, the intensity of the T_{2g} phonon mode was found to increase as CN⁻ concentration increased. Fig. 2.9 shows the integrated Brillouin peaks which have been normalized to the peak value of pure KBr as a function of CN⁻ concentration at room temperature. Such an increase may be due to the larger photoelastic constant of KCN than that of KBr.

For a transverse acoustic phonon with T_{2g} symmetry in (KBr)_{1-x}(KCN)_x, the differential Brillouin scattering cross section of eqn. (2.23) can be further written as

$$\frac{d\sigma}{d\Omega} = \frac{k_{\rm B} T \omega_0^2 V}{32\pi^2 c^4 \rho v^2} |P_{44}|^2$$
(2.27)

where P_{44} is the photoelastic constant with T_{2g} symmetry. As the CN⁻ concentration changes, the contribution to the Pockel's photoelastic constant by KBr and KCN may be determined by weighting their respective concentrations.

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Fig. 2.9 Integrated Brillouin peak counts for T_{2g} phonons as a function of CN⁻ concentration normalized to the integrated peak counts of KBr are indicated by stars. The open circles are the calculated values of the differential cross-section equation. All measurements are at room temperature.

That is

 $P_{44mix} = x P_{44KCN} + (1 - x) P_{44KBr}$ (2.28) where x is CN⁻ concentration. Combining equations (2.27) and (2.3), the ratio of the Brillouin intensity between the mixed KBr:KCN and the pure KBr crystal can be expressed as

$$\frac{I_{\text{mix}}}{I_{\text{KBr}}} = \left(\frac{xP_{44\text{KCN}} + (1 - x)P_{44\text{KBr}}}{P_{44\text{KBr}}}\right)^2 \left(\frac{\nu_{\text{KBr}}}{\nu_{\text{mix}}}\right)^2 \quad (2.29)$$

For x=0.5, the measured ratio of I_{mix}/I_{KBr} equals 23. Substituting ν_{KBr} =5.84 GHz, ν_{mix} =4.7 GHz and P_{44KBr} =-0.026 into eqn. (2.29), we obtain P_{44KCN} =-0.174. We thus deduce that the absolute value of P_{44} in KCN is seven times larger than that of KBr. Using P_{44KCN} and the phonon frequencies measured at different CN⁻ concentrations at room temperature, the theoretical intensities are calculated and shown in Fig. 2.9 as stars. Considering the experimental uncertainties such as the alignment of the tandem Fabry-Perot, the results of the theory and the experiment agree quite well.

CHAPTER 3

Quasi-elastic Scattering in $(KBr)_{1-x}(KCN)_{x}$

3.1 Background theory

In any light scattering experiment, there are two components in the scattered light: a central peak (at $\omega=0$), and side bands (at $\omega\neq0$). The side bands (or inelastic components) are produced by excitations such as acoustic phonon modes in solids, discussed for KBr:KCN in the last chapter. In this chapter, we will focus our attention on the central component in KBr:KCN. for clarity we classify the central peak into two categories: elastic and quasi-elastic.

The elastic peak, which has little relationship to the crystal structure, is usually caused by the stray light or static defect scattering, and is characterised by its temperature independent intensity. Mills⁶¹ formulated a theory of elastic scattering by point defects in pure alkali halides and found that the scattering cross section is proportional to ω_0^4 , where ω_0 is the frequency of the incident light. However, an experimental study of this peak is unavailable due to difficulties in obtaining exact

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information about defects which can be impurity ions, vacancies, color centers, and dislocations. Since the extremely strong elastic scattering intensity can mask the much weaker Brillouin component in solids, considerable effort has been made to remove or reduce this elastic peak.

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In contrast to the elastic peak, the quasi-elastic component is dependent on temperature, and plays an important role in critical structural phase transitions in crystals, such as in KTaO_3 .⁶² The width of the peak may be zero (referred to as static) or non-zero (referred to as dynamic). The origin of the quasi-elastic peak usually comes from one or more of the following three mechanisms: entropy fluctuation, phonon density fluctuation, and mobile defects.

For the case of entropy fluctuation, ⁵⁵ consider a solid described by the independent thermodynamic variables, density ρ and temperature T. A fluctuation of the dielectric constant, $\delta \epsilon$, may be expressed as

$$\delta \epsilon = \left(\frac{\partial \epsilon}{\partial \rho}\right)_{\mathrm{T}} \delta \rho + \left(\frac{\partial \epsilon}{\partial \mathrm{T}}\right)_{\rho} \delta \mathrm{T}$$
$$= \left(\frac{\partial \epsilon}{\partial \rho}\right)_{\mathrm{T}} \left(\left(\frac{\partial \rho}{\partial \mathrm{P}}\right)_{\mathrm{S}} \delta \mathrm{P} + \left(\frac{\partial \rho}{\partial \mathrm{S}}\right)_{\mathrm{P}} \delta \mathrm{S}\right) + \left(\frac{\partial \epsilon}{\partial \mathrm{T}}\right)_{\rho} \delta \mathrm{T}$$
(3.1)

where ϵ is the dielectric constant, P is the pressure and S is entropy. The first term in the bracket describes the Brillouin scattering from adiabatic sound waves (acoustic phonons), while the second term describes the quasi-elastic scattering due to entropy fluctuation (δ S). The scattering from the second term appears as a peak centered at $\omega=0$ with a width Γ given by

$$\Gamma(FWHM) = 2Dq^2 \tag{3.2}$$

where D is the thermal diffusivity and q is the wavevector of the sound wave.

For liquids, the last term of eqn. (3.1) can be ignored. The ratio of the scattered intensity in the central peak (I_C) to that in Brillouin peak (I_B) is given by the Landau-Placzek ratio

$$R_{0} = \frac{I_{C}}{2I_{B}} = \frac{C_{P}}{C_{V}} - 1 \qquad (3.3)$$

where C_p and C_v are specific heat capacity of the sample at constant pressure and at constant volume respectively.

For solids, the last term in eqn. (3.1) is by no means negligible. A new ratio R is defined by Wehner and Klein as⁶³

$$R = R_0 \left(1 + \frac{C_P}{\alpha C_V} - \frac{(\partial \epsilon / \partial T)_{\rho}}{(\partial \epsilon / \partial \rho)_S} \right)^2$$
(3.4)

where α is thermal expansion coefficient. Therefore a central peak due to entropy fluctuations is characterised by q²-dependence of the linewidth and the modified Landau-Placzek ratio in solids.

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The second mechanism in quasi-elastic scattering is due to phonon density fluctuations.⁶⁴ The central peak arises from a higher order process involving pairs of phonons. This is most simply viewed as two phonon scattering of light in which a phonon of wavevector \vec{k} is created while another with wavevector $-\vec{k}+\vec{q}$ is destroyed. The net momentum is \vec{q} and a scattering peak centered at $\omega=\vec{v}\cdot\vec{q}$ will result, where \vec{v} is the phonon group velocity. Since phonons near the Brillouin zone boundary have a high density of states and velocity v~0, a broad spectral intensity at $\omega=0$ will result.

A phonon-density fluctuation central peak is usually observed near a critical structural phase transition in a crystal. This may be understood in that there is a negligible direct scattering cross section for the phonon density fluctuation (PDF) peak, whereas the scattering is observed only indirectly via the PDF coupling to the soft mode which occurs near the phase transition. The characteristics of the linewidth of PDF central peak are that it exhibits no q-dependence and it is linearly dependent on temperature.⁶⁴

The third mechanism of quasi-elastic scattering is due to the mobile defects in solids. 65,66 When a defect ion hops among sites, the local polarizability associated with the ion will fluctuate and result in a central peak with a linewidth proportional to the hopping frequency of

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the ion. Halperin and Varma⁶⁷ have developed a theory to explain the effect of defects on the static and dynamic central peak near a critical phase transition. However, neither the identity nor the concentration of the defects in such crystals which undergo a second order phase transition can be experimentally determined,⁶⁴ Hence the Halperin-Varma model has not been quantitatively examined.

The quasi-elastic central peak is usually related to the soft mode in a crystal near the structural phase transition. The total spectrum must be analysed in terms of a coupling model developed by Fleury⁶². If two excitations (such as a quasi-elastic peak, and a Brillouin peak) are described by uncoupled susceptibilities χ_1^0 and χ_2^0 respectively, the coupled susceptibility χ can be expressed as⁶²

$$x = \frac{x_1^0}{1 - A^2 x_2^0 x_1^0}$$
(3.5)

where A^2 is the coupling strength. The scattering of light is proportional to χ , or more explicitly,

$$S(\vec{q},w) = \frac{\hbar}{\pi} [n(\omega) + 1] \operatorname{Im} \chi(\vec{q},w) \qquad (3.6)$$

where n is the Bose-Einstein factor.

The quasi-elastic central mode in $(KBr)_{1-x}(KCN)_x$ has been revealed by neutron scattering experiments⁸⁹ near an

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orientational glass "phase" transition rather than near a critical structural phase transition. The peak intensity was found to increase with decreasing T near T{f} . However, the resolution of those experiments was not sufficient to measure the linewidth of the central component. This has left unanswered whether this peak is due to static or dynamic phenomena. Here we report the measurements of the quasi-elastic central peak in (KBr) $_{1-x}$ (KCN)_x with x=0.35 and 0.5 using a high resolution tandem Fabry-Perot interferometer. We find that the width of the central peak is strongly temperature dependent and is dynamic in origin. The quasi-elastic spectra have been analysed using both Michel's microscopic susceptibility model and the phenomenological coupling susceptibility model.

Considering the evidence of the dynamic quasielastic peaks in other mixed crystals such as $Rb_{1-x}(NH_4)_xH_2PO_4$,⁶⁸ and $KTa_{1-x}Nb_xO_3$,⁶⁹ the feature of the central peak may be a universal property in glassy crystals and certainly plays an important role in the intriguing orientational glass state.

3.2 Experimental

The study of quasi-elastic scattering in solids is usually frustrated by the presence of strong elastic light scattered by static defects and inhomogeneities as

discussed in the last section. A molecular-iodine filter⁷⁰ with a resonant absorption band coinciding with the 5145 A Argon ion laser line, is usually used to remove elastic light (rejections greater than 10^7). A disadvantage of this technique, especially when used for high resolution work, is that other absorptions in the I₂ vapor introduce structure in the instrumental response which can mask features of interest in the quasi-elastic spectrum. Although a computer normalization technique⁷¹ was developed to compensate for the messy transmission characteristics of the iodine filter, this process can only give reliable estimates of width for the quasi-elastic peak down to a limit of ~1 GHz (FWHM). The narrower peak is completely masked by the iodine absorption.

By choosing a 90°-scattering geometry and by using only high quality crystals, we circumvented the need for an iodine filter, and we directly used a tandem multipass FP to investigate the quasi-elastic scattering. The basic experimental arrangement has been described in section 2.2. Here we emphasize maintaining parallelism of the FP mirrors, elimination of modulation effects in the quasielastic profile, as well as reduction of stray light. A new cryostat system including a temperature controller will be also described.

The instrument function is the spectral profile which would be observed with a purely monochromatic source.

The minimum resolvable bandwidth of the instrumental function is defined as $\Delta \nu_{BW}$ given by

$$\Delta \nu_{\rm BW} = \frac{\Delta \nu_{\rm FSR}}{F} \tag{3.7}$$

where $\Delta \nu_{\rm FSR}$ is the free spectral range and F the instrumental finesse which is the key measure of the interferometer ability to resolve closely spaced lines. The major factors which limit the finesse are (1) mirror reflectivity of less than unity; (2) lack of flatness and parallelism of mirrors. Since the mirror reflectivity and flatness are fixed, alignment of the Fabry-Perot becomes a crucial factor.

Alignment is even more important when collecting the very weak quasi-elastic scattering signal in KBr:KCN, since this requires hours of data accumulation time for a . good signal-to-noise ratio to be achieved. Such a demand can be satisfied by a computer controlled Fabry-Perot interferometer. In this system, a 4 MHz clock signal is sent to an on-board counter whose output then goes to a digital-to-analog converter (DAC) which in turn produces the signal for ramping of the translation stage. The five alignment parameters of the tandem FP (two tilt adjustments for each etalon and one for spectral overlap) are adjustable manually by varying 10-turn potentiometers and, following initial alignment, are then controlled by a computer via an eight channel DAC.

The basis of the feedback system for alignment control is through use of the integrated elastic intensity, the value of which is monitored continuously. When this drops below a prescribed percentage of an optimized initial value, a sequence of test and correction steps is initiated, varying all parameters until the height of the elastic peak is maximized, indicating that alignment is restored.

In order to minimize the resolution bandwidth, as seen in eqn. (3.7), the free spectral range should be decreased and the finesse increased. In this experiment, a very small free spectral range of typically 4 GHz was used, corresponding to a mirror spacing of 3.75 cm. At such a large mirror separation, the walk-off effect becomes significant. The beam which is parallel and near to the optical axis can be transmitted, while off-axis light will walk off after several reflections between the FP mirrors. Therefore the intensity of the stray light can be actual down. We obtained an instrumental resolution of 70-90 MHz and a finesse of about 60.

Tandem Fabry-Perots have an intrinsic weakness in that modulation effects may appear as a result of a parasitic interference, produced by the intervening space of two series connected Fabry-Perots. Such a modulation effect can seriously distort the broad quasi-elastic

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profile. The method of eliminating this effect has been published in Ref. 41. As per the argument by Vanderwal et al., if multiple back reflections within the interetaion gap have phase shifts of about 90° per cycle, wave superposition will successively cancel the modulation. A combination of a quarter-wave plate and a metallic mirror as shown in Fig. 3.1 can produce such phase changes. The arrangement in Fig. 3.1 can reduce the modulation to noise level with a signal transmission loss of only about 6%.

In order to further reduce the stray light component, samples with good optical quality are essential. Scattering from a rough crystal surface produces extremely intense reflections, light from which may mask the quasi-elastic component. The clean surfaces were obtained by cleaving the samples along (100) planes. The cleaved samples were put under vacuum as quickly as possible so that the surfaces of the crystal would not deteriorate by exposure to moisture in the air.

The sample was cooled by a continuous flow cryostat (Model DC210, CRYO Industries of Amer. Inc.) which was mounted directly above a standard liquid helium storage vessel. A small pressure was used to transfer ⁴He gas out of the storage dewar into the transfer line and directly to the sample mount. Pressure inside the storage dewar was adjusted using a herem gas cylinder containing ⁴He gas. The temperature can be varied from 4.2 K to 300 K by

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Fig. 3.1 A schematic of the tandem FP optics, showing cube corner orientation and polarization effect. All mirrors not labelled are multilayer dielectric type. (for details, see Ref. 41).

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adjusting the rate of helium flow. Additional fine temperature control was achieved by a residuance heater and a temperature controller (Model 520, Lake Shore Cryotronics, Inc.). The temperature was measured using both a thermocouple and a silicon diode.

A serious problem in temperature measurements comes from local laser heating which is difficult to estimate, since the thermometer can only be placed near the light scattering region. In order to decrease laser heating, one should make the laser power lower. However, lowering laser power results in a decrease in the intensity of scattered light, so it is necessary to compromise between the need to minimize local heating and have sufficient signal intensity. We have measured the temperature of the scattering volume by monitoring the Brillouin shift which is a sensitive function of temperature near the orientational glass transition.

The polarization character of the quasi-elastic scattering component was investigated by the following arrangement. The (100) surface of the sample was perpendicular to the incident beam and the (010) surface perpendicular to the scattering light. The incident beam was polarized along [001] direction, while the scattered light polarized in either [001] or [100] direction was collected by changing a polarizer in front of the Fabry-Perot interferometer.

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3.3 Results and discussion3.3.1 Spectral analysis

In light scattering experiments, the scattered light, T(t), was analysed by an optical and electronic system which is characterized by an instrumental function R(t,t'). The measured signal, M(t), is a convolution of the instrumental function and the "true" signal T(t) and is given by the convolution integral⁷²

$$M(t) = \int_{-\infty}^{\infty} R(t - t') T(t') dt' \stackrel{\sim}{=} (3.8)$$

The ideal instrumental function for a multi-pass Fabry-Perot interferometer can be described by the Airy function to the power n, where n is the number of passes. In practice the detailed shape of the instrumental function is modified by the size of the pinhole, parallelism of the FP mirrors, photon counting process, etc. Therefore the instrumental function used in this investigation was measured as the response of the whole spectral collecting system to the laser light. Mathematically if T(t) is a δ function, eqn. (3.8) yields

$$M(t) = \int R(t - t') \, \delta(0) \, dt' = R(t) \quad (3.9)$$

Thus assuming that the laser beam has zero linewidth, the

measured elastic peak equals to the instrumental function.

We chose the elastic peak, collected at either high temperature (T>90K) or low temperature (T<40K) in $(KBr)_{1-x}(KCN)_x$, as an instrumental function, since there was negligible contribution from the quasi-elastic scattering to the elastic component in such temperature ranges (we will discuss this latter).

Although controlled by a computer, the alignment of the tandem Fabry-Perot has slightly changed from day to day which results in varying of the instrumental function. In order to obtain such a function that truly represents the response of the system at a certain period of time. We took an instrumental spectrum for every series runs.

The extraction of the original signal T(t) from the measured (or distorted) signal involves inversion of the integral eqn. (3.8) and is referred to as deconvolution. Because of spectral noise, this is an ill posed problem due to the existence of a large set of possible solutions, all satisfying eqn. (3.8) to within experimental error of measured signal M(t).^{73,74} The challenge of obtaining unique solution for deconvolution has led to many papers on this subject.^{73,74}

We have tried using three different deconvolution techniques to analyse the quasi-elastic spectra in $(KBr)_{1-x}(KCN)_x$; a Baysian probability method, ⁷² a spline function method⁷⁷ and a constrained regularization

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method.^{73,74} The programming code of the first has been written in this laboratory.^{75,76} The second and third are available in FORTRAN packages called DECOSP⁷⁷ and CONTIN^{73,74} respectively. For our purpose we found these techniques useful to obtain the phonon lineshape from the Brillouin component, but all failed to extract quasielastic scattering from the elastic peak. The wing of the deconvoluted elastic peak showed many oscillations which masked the detailed shape caused by the quasi-elastic scattering. This may be because these deconvolution methods cannot handle the extremely sharp and strong elastic peak whose peak intensity is about six orders of magnitude larger than the intensity of the quasi-elastic wing.

Alternatively we directly used the convolution algorithm to calculate eqn. (3.8). The assumed form of a true signal T(t) is convoluted with a instrumental function R(t-t') and the result is used to fit a measured signal M(t). The advantage of this method is that there were no oscillations in the wing of the true signal, while the disadvantages are that the priori knowledge of the true signal is needed and fitting process is rather time consuming.

3.3.2 Quasi-elastic scattering

Fig. 3.2 and Fig. 3.3 show typical quasi-elastic Brillouin spectra at various temperatures for x=0.5. The dotted lines are experimental data which consist of a quasi-elastic wing and an anti-Stokes transverse acoustic phonon peak. For clarity the strong elastic peak at $\omega=0$ was removed from the spectra. The solid lines are fitted curves which will be discussed latter.

The spectra shown have the same intensity at the center of the elastic peak (at frequency $\omega=0$). The differences in intensity of the quasi-elastic wings at different temperatures are very clear. At freezing temperature $T_f=80$ K (for x=0.5) the quasi-elastic peak is very broad and it narrows rapidly with decreasing temperature. Below 50 K the quasi-elastic peak can no longer be resolved. On the other hand, at T>85 K the quasi-elastic peak becomes so broad that it cannot be distinguished from the background. Similar results were obtained for x=0.35 as shown in Fig. 3.4 and Fig. 3.5.

The spectra shown in Fig. 3.2 - Fig. 3.5 were taken in X(ZX)Y scattering arrangement. For X(ZZ)Y geometry, the quasi-elastic component was much weaker. Therefore the polarization selection rule of the central peak is consistent with the soft transverse acoustic phonon, which has a $T_{2\sigma}$ symmetry and only shows up in X(2X)Y arrangement.

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Fig. 3.2 Quasielastic-Brillouin spectra of $(KBr)_{0.5}(KCN)_{0.5}$ at T=81 K, 72 K, 64 K and 30 K. Dotted lines are experimental data and solid lines are fitted curves. The spectrum at 30 K was used as a resolution function.





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The detailed study of the soft phonon has been discussed in the last chapter. Here we note that the integrated intensity of the phonon peak decreases with temperature at $T < T_{f}$, which indicates a transfer of intensity into a central peak. This phenomenon has also been observed in a mixed ferroelectric antiferroelectric system.⁶⁸

The solid lines in Fig. 3.2 - Fig. 3.5 are fitted curves which are the result of a convolution of the instrumental function and a "true" signal. The detailed discussion of convolution has been given in 3.3.1. The instrumental function for each set of spectra from Fig. 3.2 to Fig. 3.5 has been identified in the figure captions. The "true" signal profile was assumed to consist of three components: a delta function at $\omega=0$ which was due to a stray light and extraneous elastic scattering from static defects, a broad Lorentzian quasi-elastic peak centered at $\omega=0$, which is of interest here, and a Lorentzian shaped phonon peak. The heights of the three components, the widths of the quasi-elastic and phonons peaks, and the phonon frequency were left as adjustable parameters. The results of the best fit are listed in table 3.1 for x=0.35 and 0.5 respectively. This treatment provides a highquality fit to the main features of the spectra as may be seen in Fig. 3.2 - Fig. 3.5.

Logarithmic plots of the width (FWHM) of the quasielastic peak for x=0.35 (circle) and x=0.5 (star) against

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BKG - background, and a.u. - arbitrary unit. Delta heights for x=0.5 and Q - quasi-elastic peak, B - Brillouin peak, H - height, W - width (FWHM), Summary of parameters for fitting quasi-elastic Brillouin spectra, where ţ, x=0.35 are about 1.3x10⁵ and 1.4x10⁵ respectively. P Table 3.1

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B. Shift (GHz)	1.88	1.80	1.85	2.00	2.48	3.15	3.21	3.48	3.62	•	
BKG (a.u.)	0.03	0.04	0.10	0.25	0.40	0.10	0.22	0.12	0.12		
В.Н. (а.u.)	3.80	3.25	2.80	1.62	0.85	2.40	2.85	1.60	2 60		
B.W. (GHz)	0.602	0.890	0.942	0.759	0.471	0.508	0.411	0.333	0.284		
Q.H. (a.u.)	0.7	1.7	2.8	3.8	. 11.0	1.0	2.9	4.0	0.6		
Q.W. (GHZ)	1.960	1.465	1.099	0.500	0.180	1.420	0.617	0.315 4	0.139		>
т (К)	84	81	LL	72	64	65	60	55	50		
X (mole%)	0.5	,	• • •			0.35		,			·

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1/T are shown in Fig. 3.6. The best fit was obtained with

	ν	=	7.9	х	10 ¹²	exp[-562/T]	for	x=0.35	(3.10)
and	ν	=	2.8	x	10 ¹²	exp[-612/T]	for	x=0.5	(3.11)

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The activation energies and attempt frequencies in eqn. (3.10) and (3.11) are in good agreement with those obtained by dielectric measurements.^{19,28} Therefore we believe that the quasi-elastic scattering revealed the CN⁻ dipolar relaxation process. ν represents the most probable reorientation rate which decreases as temperature decreases, following an Arrhenius law.

In light scattering measurements, the intensity of the scattered light is proportional to the Fourier transform of the correlation function of the polarizability i.e.

$$I(\omega) = \frac{A}{2\pi} \int_{-\infty}^{\infty} \langle \alpha(t) | \alpha(0) \rangle e^{i\omega t} dt \qquad (3.12)$$

where $\alpha(t)$ is the sample polarizability tensor and is a function of the displacements and orientations of the ions in the scattering volume.⁷⁸ Each CN⁻ ion is characterized by a polarizability tensor with the components $\alpha_{||}$ and α_{\perp} , where || stands for the direction parallel to the CN⁻ dipolar axis, \perp for the direction perpendicular to the axis (for details, see section 4.3). The CN⁻ reorientation results in fluctuations of the polarizability and leads to



a quasi-elastic scattering component.

Fig. 3.7 shows the intensity of the quasi-elastic peak at $\omega=0$ versus $1/T^2$ for x=0.35 and x=0.5. The linear relation is evident and may be understood by Michel's theory.³⁹

Michel has used a symmetry adapted spherical harmonic function Y_{α} to describe the orientational motion of the CN⁻ ion. In an orientational glass state the thermal average (denoted by < >) of Y_{α} at a site \vec{i} is non-zero, i.e.

$$\langle \mathbf{Y}_{\gamma}(\vec{\mathbf{x}}) \rangle \neq 0$$
 (3.13)

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while the configurational average (denoted by []) of this quantity vanishes, i.e.

 $[\langle Y_{\alpha}(\vec{\ell})] = \frac{1}{N_{\chi}} \sum_{\vec{\ell}} \tau(\vec{\ell}) \langle Y_{\alpha}(\vec{\ell}) \rangle = 0 \qquad (3.14)$

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where N_{χ} is the total number of CN^{-} ions in the crystal with CN^{-} concentration $x=N_{\chi}/N$, and $\tau(\vec{t})$ has value 1 where there is a CN^{-} at site \vec{t} and value 0 when the CN^{-} is replaced by a Br⁻ ion. A glass order parameter is further defined as

$$\nu = [\langle Y_{\alpha}(\vec{z}) \rangle^{2}]$$
 (3.15)

and can be explicitly expressed as

$$\psi = x(1 - x) y_{w}^{2} \frac{h^{2}}{T^{2}}$$
(3.16)

where x is the CN^- concentration. T is temperature, Y_w represents a parameter of CN^- orientational correlation and is weakly temperature dependent. h is the strength of the random strain field which is caused by the different radii between Br^- and CN^- ions.

Starting from a dynamical description of translation rotation coupling and random field-rotation coupling,³⁹ Michel has formulated the neutron scattering law. The essential point of the scattering law is that in addition to the inelastic acoustic mode, there is an elastic scattering component whose differential cross section is proportional to the glass order parameter, i.e.

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \propto \psi_{(0)} \tag{3.17}$$

Since below T_f , ψ increase monotonically with decreasing T^2 as described in eqn. (3.16), the intensity of the corresponding quasi-elastic peak should increase as $1/T^2$.

From the slopes of the linear fitting lines in Fig. 3.7, we obtain $h(x=0.5)/h(x=0.35)^{-1.5}$. This value suggests that the random field on the orientational motion of CN⁻ ions for x=0.5 is stronger than one for x=0.35 as

expected. As discussed before the random field is due to the difference in the ionic radii of the substitutional ions. Therefore at the x=0 and 1 limit, the random field should be zero, and be a maximum at x=0.5. The T_{\star}^{-2} behavior of ψ which leads to a divergence of the central peak at T=0 is no longer valid at low temperature (<30 K), where a quantum mechanical calculation is required rather than classical statistical mechanics used here.

From our investigation, the central peak exhibits a strong temperature dependent linewidth and must be dynamic in origin. Comparing the results of neutron and light scattering, we suggest there may be two contributions to the central peak: first of all, at temperature below T_f , the elastic interaction between the cyanide quadrupoles tends to freeze their axes into a particular configuration. The static strain, which accompanies such local freezing in cyanide quadrupoles, results in a static central component. Secondly, since the CN electric dipoles remain free to flip over below T_{f} , there will also be a dynamic scattering central component. This picture has a close link to the theory of Halperin and Varma.⁶⁷ They classified the defects in solids into relaxing and frozen types. The frozen defects cause elastic scattering with a zero linewidth of static central mode, while the relaxing defects lead to a dynamic central mode whose linewidth is proportional to the hopping rate for defects moving among

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quasi-equal energy positions. Michel also separates the central mode into a static part (due to a breaking of local symmetry) and a dynamic part (due to time-dependent orientational fluctuations). But an analytic solution of the dynamic part has not yet been formulated.

We have attempted to use the coupled susceptibility $model^{64,79}$ to analyze the experimental spectra. In this model the susceptibility χ is expressed as^{79,80}

$$\chi^{-1}(\omega) = \omega_{a}^{2} - \omega^{2} - 2i\omega\Gamma_{a} - \frac{\gamma\delta^{2}}{\gamma - i\omega}$$
(3.18)

where the first three terms describe an uncoupled acoustic phonon (oscillator) with frequency ω_a and damping Γ_a . The last term provides coupling of strength δ to a central mode with a Debye relaxation rate γ . The spectral profile for this coupled mode pair is thus given by ^{79,80}

$$S = \frac{h}{\pi} [\pi(\omega) + 1] \operatorname{Im} \chi(\omega) \qquad (3.19)$$

where $n(\omega)$ is the Bose-Einstein thermal factor. An attempt was then made to fit the quasi-elastic Brillouin profile by convoluting the instrumental function with the results calculated via eqns. (3.18) and (3.19). Here the values of ω_a and Γ_a were obtained from a Brillouin peak taken at room temperature where, it is assumed, no coupling occurs. δ ' and γ were treated as free fitting parameters; however, it

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proved impossible to fit the data. δ could be adjusted to yield the correct renormalized phonon frequency, but if γ was chosen to yield the correct phonon width, the quasielastic peak was too narrow. Conversely, if the quasielastic peak was fitted, the calculated phonon would be about two times broader than the experimental one.

This suggests that the quasi-elastic central peak, and the phonon broadening and renormalization are mainly due to two different processes. From activation energies , obtained from the Arrhenius plot in Fig. 3.6 it seems that the central peak is due to scattering by the electric dipole. The analysis in Chapter 2 suggests that the phonon, on the other hand, is affected mainly by the elastic properties of the CN^- ion.

In conclusion, we have observed a dynamic central peak in $(KBr)_{1-x}(KCN)_x$. the temperature dependence of the linewidth of this peak follows an Arrhenius law. We consider this peak to be due to the dynamic process of the CN dipole reorientation.

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CHAPTER 4

Polarization Anomalies in $(KBr)_{1-x}(KCN)_x$ Under a Uniaxial Stress

4.1 Introduction

The CN^{-} ion in $(KBr)_{1-x}(KCN)_{x}$ has a small electric dipole moment (μ =0.07 eÅ) and an elastic quadrupole moment due to its ellipsoidal shape (major and minor semi-axes ~2.15 Å and 1.78 Å respectively).⁸¹ As a result the CN^{-} ion can'interact with both an electric field and elastic stress. The interaction energy of (E_{ele}) the electric dipole ($\vec{\mu}$) with an applied electric field (\vec{E}) can be expressed as

 $\begin{cases} E_{ele} = -\Sigma \ \mu_{i} \ E_{i} & (i = 1, 2, 3) \\ i & . \end{cases}$ (4.1)

By analogy to the electric dipole, the interaction energy of an elastic quadrupole with a stress field, $\ddot{\sigma}$, is given by⁸²

$$E_{elas} = -v_{0} \sum_{ij} \lambda_{ij} \sigma_{ij} \qquad (4.2)$$

] where v_0^{λ} is the atomic volume of the host crystal, and λ_{ij}

is a second rank matrix which describes the elastic quadrupole.

Since the average size of the cyanide ion is similar to that of the bromine, mixed crystals $(KBr)_{1-x}(KCN)_x$ can be made over the entire range from the dilute case, x=0, to the pure KCN limit, x=1. The behavior of $(KBr)_{1-x}(KCN)_{x}$, we under application of stress or an electric field, has been previously studied in the two extreme cases outlined above.

In pure KCN, the CN⁻ ions are free to rotate at high-temperature and the structure is cubic. When the temperature is lowered to 168 K, the KCN crystal undergoes, a first order phase transition to an orthorhombic structure in which the CN⁻ ions are aligned along the <110> directions in a ferroelastic state. The onset of this transition is marked by the appearance of domains, and optical bacity. By application of uniaxial stress in the ferroelastic phase, Durand et al.⁸³ have succeeded in aligning a fraction of the elastic domains in one direction and have observed partially polarized Raman spectra. By varying the stress and light scattering geometries, Durand et al.⁸³ have determined the symmetry properties of the Raman active modes in KCN.

In the dilute case, the CN⁻ ions rotate in a very shallow octahedral crystal field with minima in the eight <111> directions. Therefore the CN⁻ behavior can be easily affected by external perturbations. Under application of a

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uniaxial stress, high resolution infrared spectroscopy⁸⁴ has revealed stress-induced splitting of CN⁻ tunneling levels which are otherwise degenerate. The CN⁻ electric dipoles can also be partially aligned along the direction of the applied electric field at low temperatures.⁸⁵ The alignment of the CN⁻ dipoles results in an anisotropy in the optical properties of the originally optically isotropic crystal, whereby the crystal becomes doubly refracting (Kerr effect). The study of this effect by Luty et al.⁸⁵ showed that the behavior of the CN⁻ alignment is paraelectric and follows Curie's law.

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When approaching the intermediate CN^- concentration range (0.01<x<0.6), a complex situation is encountered. In this regime, there are strong interactions among CN^- ions so that, in contract to the dilute case, Curie's law which neglects the CN^--CN^- interactions may not be valid; nor are there, unlike pure KCN, any observable elastic domains. To our knowledge no stress or electric field related experiments in this CN^- concentration range have been reported.

Herein we present the results of stress-induced Brillouin scattering anomalies at CN^- concentrations of x=0.35, 0.5 and 0.6. We have found that certain strong Brillouin spectral components appeared in a symmetry forbidden polarization under a uniaxial stress.

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4.2 Experimental

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The experimental arrangement used for this measurement is as similar as shown in Fig. 2.1. The light source used was an Argon ion laser. The scattered light was analysed with a single Fabry-Perot interferometer in two-pass configuration.

The laser beam was incident along the [100] axis of the KBr:KCN crystal with its polarization along the [001] axis. The scattered beam was located along the [010]axis with its polarization along the [001] or [100] direction. These two scattering arrangements can be expressed as X[ZZ]Y and X[ZX]Y respectively, and will be referred to, using the conventional notation, as VV and VH.

The highly polarized incident beam was achieved using a laser-polarizing cube, which was made of pairs of right angle prisms cemented together, and separated by a special multilayer dielectric film. The polarization of the scattered light was examined by a sheet polarizer with extinction ratio better than 1 part in 1000 and a transmission of over 95%. This polarizer was mounted in a rotary head, thus permitting any desired angle of polarization to be chosen.

Stress was applied along the [001] axis of the sample with a spring loaded screw. In order to prevent plastic deformation the applied stress should be less than 10 kg/cm². The magnitude of stress was measured at room temperature for each run. Some uncertainty in the absolute value of the stress may have resulted upon cooling, due to the different thermal expansion in the sample and the sample holder.

The sample was kept under vacuum in a continuous flow helium cryostat, wherein, temperature was monitored by both a diode thermometer and a thermocouple. For a more detailed description refer to Section 3.2 of Chapter 3.

4.3 Results and Discussion

The intensity of the Brillouin scattering is proportional to $|\vec{e_s} \cdot \vec{\beta} \cdot \vec{e_i}|^2$ (for details, see section 2.3.3), where $\vec{e_i}$ and $\vec{e_s}$ are respectively incident and scattered light polarization vectors, and \vec{P} is the Pockel's matrix which has been tabulated for various crystal symmetries and light scattering geometries.⁶⁰ In this case the sample has cubic symmetry, and a 90°scattering arrangement is employed.

Considering the VH polarization configuration, the Brillouin intensity (I_{VH}) scattered from the longitudinal acoustic phonons along [110] direction can be written as

$$\mathbf{I}_{VH}^{L} \alpha |\mathbf{e}_{i} \cdot \mathbf{p} \cdot \mathbf{e}_{s}|^{2} = \left(\begin{bmatrix} 001 \end{bmatrix} \begin{bmatrix} \mathbf{P}_{11} + \mathbf{P}_{12} & 2\mathbf{P}_{44} & \mathbf{0} \\ 2\mathbf{P}_{44} & \mathbf{P}_{11} + \mathbf{P}_{13} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{P}_{12} - \mathbf{P}_{13} \end{bmatrix} \begin{bmatrix} \mathbf{1} \\ \mathbf{0} \\ \mathbf{0} \end{bmatrix} \right)^{2}$$

For the VV configuration, we find

$$I_{VV}^{L} \alpha |P_{12} - P_{13}|^2$$

The Pockel's matrices⁶⁰ for the transverse acoustic phonons along the [110] direction, with T_1 (or Eg) and T_2 (or T_{2g}) symmetries, are expressed as

$$\overset{P}{P_{T1}} = \begin{pmatrix} P_{11} - P_{12} & 0 & 0 \\ 0 & P_{12} - P_{11} & 0 \\ 0 & 0 & 0 \end{pmatrix} \text{ and } \overset{P}{P_{T2}} = \begin{pmatrix} 0 & 0 & P_{44} \\ 0 & 0 & P_{44} \\ P_{44} & P_{44} & \delta \end{pmatrix}$$

respectively. By the way of a calculation similar to that

$$I_{VV}^{T2} = 0, \quad I_{VH}^{T2} \alpha |P_{44}|^2$$

and $I_{VV}^{T1} = I_{VH}^{T1} = 0$

The selection rules are thus completely determined by the $|\hat{e}_i \stackrel{p}{\neq} \hat{e}_s|^2$ term. For the KBr:KCN cubic system in our scattering arrangement, the VV spectrum should contain only a longitudinal acoustic phonon peak (LA) and the VH spectrum only a T_{2g} transverse acoustic phonon peak (TA). The T_1 acoustic phonon is forbidden for both VV and VH spectra.

Measurements with the VV and VH configurations have been performed on stress-free samples with x=0.35 and 0.5 from 30 K to room temperatures. The polarization selection rules were found to hold. This is not surprising, since below a critical CN⁻ concentration, x⁻0.6, KBr:KCN do not undergo the cubic to orthorhombic phase transition. Instead, the CN⁻ ions freeze into an orientational glass state as the temperature is lowered, while the lattice structure remains cubic.⁶

Under an external stress of 10⁵Pa along the [001] direction, Brillouin spectra for pure KBr and for x=0.2 at temperature ranging from 30 K to 295 K did not reveal any polarization anomalies. A typical spectrum taken at room temperature for KBr is shown in Fig. 4.1. Room temperature spectra of x=0.35, 0.5 and 0.6 also contained no polarization anomalies as illustrated in Fig. 4.2 for the x=0.5 sample. However, as the temperature was lowered, the polarization of the Brillouin peaks changed dramatically for the stressed samples with $0.35 \le x \le 0.6$. There were no observable changes in phonon frequency and linewidth induced by the stress.

Fig. 4.3 shows typical VV and VH spectra for x=0.5 at T=120 K. The symmetry forbidden LA peak appears in the VH spectrum and TA mode in the VV spectrum. We will refer

Fig. 4.1 The VV (solid) and VH (dashed) Brillouin spectra for pure KBr under a stress of 10⁵ Pa along [001] at room temperature. The symbols S and AS refer to the Stokes and anti-Stokes peaks respectively.

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Fig. 4.3 The VV (solid) and VH (dashed) Brillouin spectra for x=0.5 under the same stress at 120 K. The free spectral range was 19.8 GHz. For visual clarity, the VH spectrum has been shifted vertically. The backgrounds of VV and VH spectra should be identical.

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to the intensities of the TA mode occurring in VH and VV spectra as I_{VH} and \hat{I}_{VV} respectively. The typical ratio of I_{VV}/I_{VH} for x=0.35, x=0.5 and x=0.6 against temperature, under [001] stress of 10⁵ Pa, are shown in Fig. 4.4. The anomalous TA component in the VV spectra first occurred at around 120 K for x=0,35, 160 K for x=0.50, and at 180 K for x=0.6. The magnitude of this ratio increased with decreasing temperature, reaching a maximum at an average of 75 K for x=0.35, 100 K for 0.5 and 125 K for x=0.6. Increasing stress produced more pronounced anomalies. The ratios I_{VV}/I_{VH} under a stress of 8×10^5 Pa for x=0.35 and 0.6 are shown in Fig. 4.5. The polarization mixing even occurred at room temperature for x=0.6. The occurrence of the forbidden I was reproducible around certain temperatures. However the absolute values of I_{VV}/I_{VH} and the position of the maximum of the ratio varied from one run to the next due to changes in the location of the focussed laser beam in the sample; hence, Figs. 4.4 and 4.5 represent averages over many experiments.

There are two reasons to suggest that CN^- ions favor alignment along [110] axes when under [001] stress. Firstly, when pure KCN undergoes a cubic to orthorhombic structural phase transition, CN^- ions are aligned along [110] and form ferroelastic domains,⁴ which indicates that [110] is the easier direction for collective alignment of CN^- ions. So also KBr-KCN alloys tend to change from

Fig. 4.4 A typical ratio between the intensity of TA modes in the VV (forbidden) and in the VH (allowed) polarizations, for x=0.35 (0), x=0.5 (*), and x=0.6 (+) under a stress of 10^5 Pa, is plotted against temperature.

 $(f^{(k)})^{*}$


Fig. 4.5 A typical ratio between the intensity of TA modes in the VV (forbidden) and in the VH (allowed) polarizations, for x=0.35 (0) and x=0.6 (+) under a stress of $8x10^5$ Pa, is plotted against temperature.



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"cubic" to "orthorhombic" symmetry under a uniaxial stress. Therefore the CN⁻ ions favor alignment along [110]. Secondly, in the intermediate CN⁻ concentration, CN⁻ ions may form pairs,⁸⁶ triplets,⁸⁶ even domains.^{87,26} A possible lowest energy configuration of CN⁻ pairs is that CN⁻ ions are in the <110> direction and "nod" toward each other;⁸⁶ that is, the dipole pair axes converge, in contrast to a dipole pair with parallel axes.

,Each CN⁻ ion has a polarizability tensor α with different components parallel $(\alpha_{||})$ and perpendicular (α_{\perp}) to the dipole axis.⁸⁵ The refractive index (n) is related to the average polarizability by the Lorentz-Lorenz formula⁸⁵

$$\alpha = \frac{3}{4\pi N} \frac{n^2 - 1}{n^2 + 2}$$
(4.3)

Cyanide ions have sizable elastic dipoles.⁴ A [110] orientation for these elastic dipoles will be favored by a [001] stress and will result in a difference in refractive index

 $\Delta n = n_{||} - n_{\perp} \propto (\alpha_{||} - \alpha_{\perp}) \ F \ (P, T, \sigma_{a}, \sigma_{i}) \qquad (4.4)$ • where F is a CN⁻ partial alignment function which depends on the CN⁻ elastic dipole moment P, temperature T, appfied stress σ_{a} , and stress σ_{i} caused by CN⁻-CN⁻ interaction. This birefringence Δn introduces a phase shift between the scattered light components parallel and perpendicular to

the direction of CN⁻ alignment given by^{85,88}

$$\delta = \frac{2\pi d}{\lambda} \Delta n \qquad (4.5)$$

where λ is the wavelength of light, d is the optical path length. The phase shift produces elliptical polarization of the emerging light. The weak birefringence effect due to partial alignment of CN⁻ ions under stress was observed in the Brillouin component but not in the elastic peak. The reason is that the Brillouin peak⁹ is scattered light whose polarization is determined by the Pockel's matrix, while the elastic peak is unpolarized scattered light produced by static defects and surface scattering. It is obvious that the birefringence has no effect on the unpolarized light.

With decreasing temperature thermally_activated randomization decreases, while more CN^- ions are aligned by a uniaxial stress. Hence the normally VH polarized TA mode gradually becomes elliptically polarized. This polarization was verified by use of a rotating polarizer and a quarterwave plate. Thus a TA peak appears in VV spectra and an LA peak in VH spectra at lower temperatures, and the I_{VV}/I_{VH} ratio increases. As the temperature decreases further, a very fine pattern of ferroelastic domains may begin to form: these have been observed in pure KCN crystals.⁸⁹ The random nature of the domain structure,

i.e. each domain may not be aligned in the same direction, would decrease the $I_{\rm VV}/I_{\rm VH}$ ratio and the ratio would exhibit a maximum.

The diameter of the scattering volume was reduced from 209 μ m to 32 μ m by changing the focal length of the focussing lens. However the general behavior of the I_{VV}/I_{VH} ratio remained the same. Therefore, if ferroelastic domains exist the size of the aligned domain under such a stress must be less than about 30 μ m. The maximum value of I_{VV}/I_{VH} increases with increasing CN⁻ concentration and stress. This can be easily explained, since the birefringence effect is dependent on the number of CN⁻ ions aligned.

The ratio I_{VV}/I_{VH} is also dependent of the phase shift which in turn depends on the stress as shown in eqn. (4.4) and (4.5). The I_{VV}/I_{VH} ratio was observed to vary with position of the laser beam in the sample. This may be due to a non-uniform distribution of stress, caused by thermal contraction of the sample and sample holder. Resultant variations in stress and position could lead to the lack of reproducibility we have observed:

In summary, we have observed elliptically polarized transverse acoustic phonon peaks in $(KBr)_{1-x}(KCN)_x$ under uniaxial stress using Brillouin light scattering. This symmetry forbidden scattering may be explained by a stressinduced partial CN^- elastic dipole alignment, which causes

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a weak birefringence effect and has significant influence on the polarization of the Brillouin scattering components.

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CHAPTER 5

Double Relaxation Processes in (KBr)_{0.5}(KCN)_{0.5}

5.1 Introduction

The occurrence of a primary or α -process and a secondary or β -process in amorphous solids can be generally observed by dielectric and mechanical relaxation spectroscopy.^{90,91} In these systems the β -relaxation exhibits an Arrhenius type of behavior and appears far below T_{σ} , the glass transition temperature, while the α relaxation often follows a Vogel-Tamman-Fulcher law and occurs near T_{α} . Surprisingly similar behavior has been observed in (KBr) $_{1-x}$ (KCN) $_{x}$, an orientational glass crystal.^{28,29}. The clearest evidence comes from the torsion pendulum measurement. In that experiment²⁹ there were two well defined peaks occurring in the internal friction loss data as a function of temperature at a frequency of 100 Hz. The primary peak at 75 K was interpreted in terms of quadrupolar relaxation, while the secondary one at 30 K in terms of electric dipolar relaxation.

Here, an attempt was made to simultaneously observe

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the double relaxational peaks in either Brillouin or dielectric spectra.

Dielectric properties of $(KBr)_{1-x}(KCN)_x$ have been investigated by several groups.¹⁷⁻¹⁹ The real (ϵ') and imaginary (ϵ'') part of the dielectric permittivity have been measured as functions of frequency, temperature and CN^- concentration. In this investigation, we extend previous work to lower temperatures (~1 K), with particular emphasis on the temperature region above and below the dielectric loss peak at ~30 K for the x=0.5 sample. Since the relaxation regions are better resolved in plots of - $\tan\delta(=\epsilon''/\epsilon')$ rather than of ϵ'' ,⁹² due largely to the sharper peaks observed in the former, we directly measured and presented data in terms of $\tan\delta$.

It is well known that both α and β processes lead to a change in slope of the Brillouin shift versus temperature.⁹³ Considering the weakness of the possible change for the dipolar relaxation, we repeated the previous Brillouin measurements at much smaller temperature steps than before. In addition, a very small laser power (~10 mW) was used in order to prevent any temperature error introduced by laser heating.

5.2 Experimental

The capacitance and dielectric loss factor of the sample were measured using a General Radio 1615 A transformer ratio arm bridge. A sine wave generator was used as a variable frequency power source to drive the bridge. The output signal of the bridge was selectively enhanced by a Rohde and Schwarz tunable amplifier. A Hewlett-Packard oscilloscope served as a null detector. The measured values of capacitance and $\tan \delta$ (dissipation factor D times operation frequency) were accurate to within 0.1 and 0.01 respectively.

The $(KBr)_{0.5}(KCN)_{0.5}$ crystal was cleaved along the (100) planes with a section of 11x4 mm² and a thickness of 1.4 mm. The cleaved sample had a very clean surface and care was taken to prevent hygroscopic damage. Silver electrodes were evaporated onto each side of the sample under vacuum. Copper connector wires were then glued onto these two electrodes with silver paste. Insulating teflon tape was wound around the sample and its connection wires. This assembly was then shielded by an aluminum foil which was connected to the ground. All connections were made with coaxial cables in order to minimize noise.

The sample was mounted in the end of a long thin

wall stainless tube which was inserted into a liquid helium dewar (Model USHE3OA, MVE Cryogenics Co.). Temperature was varied by adjusting the distance between the sample and the liquid helium surface. With this arrangement, approximately 15 minutes were needed for equilibrium temperature to be reached. The lowest available temperature is about 1.2 K attained by pumping on the liquid helium.

An Au:0.07% Fe - chromel thermocouple was kept in contact with the sample with its reference junction in liquid nitrogen. Au:Fe - chromel was used since its change in emf (~11.33 μ V/K) is much higher than that (~1.48 μ V/K) for a common Copper-Constantan thermocouple in the temperature range from 1.2 K to 4.2 K. However care must be taken in handling this Au:Fe wire which is very easily broken.

The Brillouin profile of $(KBr)_{0.5}(KCN)_{0.5}$ was measured by a tandem Fabry-Perot interferometer in two-pass configuration. Phonon frequency was an average of the Stokes and anti-Stokes shifts. Detailed techniques have been described in Section 2.2.

5.3 Results and discussion

It is known that the slope of the acoustic phonon frequency (ν) versus temperature at constant pressure (P), $(\partial \nu / \partial T)_{\rm P}$, is related to the thermal expansion coefficient, $\alpha = 1/\Omega (\partial \Omega / \partial T)_{\rm P}$, by the expression⁹³

$$\frac{1}{\nu} \left(\begin{array}{c} \frac{\partial \nu}{\partial T} \end{array} \right)_{P} = -\gamma \quad \frac{1}{\Omega} \left(\begin{array}{c} \frac{\partial \Omega}{\partial T} \end{array} \right)_{P} \quad (5.1)$$

where γ is the Grüneisen constant and Ω is the volume. Since the thermal expansion coefficient α usually experiences a well defined step near a freezing temperature,⁹⁴ a change of slope $(\partial \nu / \partial T)_p$ should result.

Fig. 5.1 shows the T_{2g} phonon frequency as a function of temperature. From this figure there is no evidence of any change of the slope apart from the one at ~80 K, the quadrupolar freezing temperature. Specifically, there is no kink in the phonon frequency around 30 K, at which the CN⁻ dipoles were frozen in as measured by dielectric technique. This result may be understood as follows.

The freezing in of CN⁻ dipoles is a continuous process upon cooling. Depending on the frequency of the probe, the CN⁻ dipoles may or may not appear frozen. As



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the probe frequency increases, the freezing will occur at higher temperatures.²⁸ For x=0.5 samples CN⁻ dipoles freeze at ~30 K at the kilohertz range.²⁸ If dielectric measurements were performed in the gigahertz range, CN⁻ dipoles would freeze at ~80 K by an Arrhenius extrapolation.²⁸ Therefore the Brillouin scattering cannot resolve dipolar and quadrupolar relaxation processes which happened to superimpose at T~80 K in the gigahertz frequency range.

The capacitance C_p and tan δ of the $(KBr)_{0.5}(KCN)_{0.5}$ were directly read from the high precision bridge. They are related to the real and imaginary parts of the dielectric permittivity by expressions

$$c_{0} = \frac{C_{P}}{C_{0}}$$
 (5.2)

and

 $\epsilon'' = \epsilon' \tan \delta$

where C_0 is the geometric capacitance determined from the sample surface area and thickness and is about 0.278 pF for the sample used in this measurement. Following the argument given in section 5.1, we present our results using tand rather than ϵ'' .

Fig. 5.2 shows $\tan \delta$ of $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ against temperature at frequencies of 1 KHz and 10 KHz. The capacitance which is related to ϵ' is also shown in Fig. 5.3 for comparison. The general behavior is very similar

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(5.3)

Fig. 5.2 The dielectric loss tangent of

 $(KBr)_{0.5}(KCN)_{0.5}$ against temperature at 1 and 10 KHz frequency. The inset shows an internal friction curve obtained by the torsion pendulum measurement (after Ref. 6).



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to results previously reported:¹⁷⁻¹⁹ there is a dramatic drop in C_p and a dielectric loss peak around the dipolar freezing temperature of ~30 K. The position of the maximum of the tan δ shifts to higher temperature as frequency increases from 1 KHz to 10 KHz. There is only one loss peak in the temperature range from 1.2 K to room temperature. Specifically there is no evidence of a loss peak around T=75 K which is associated with the quadrupolar freezing.

It is clear that the dipolar freezing causes an elastic loss peak in the pendulum experiment, 29 while the quadrupolar freezing does not lead to an electric loss peak in dielectric measurements. This fact may be due to the temperature dependence of the dipole-quadrupole (D-Q in short) coupling. The freezing of the quadrupolar occurs at rather high temperature ("80 K for x=0.5) where the D-Q coupling is weak. Therefore the dielectric measurement cannot detect the quadrupolar relaxation behavior and only reveal one loss peak due to the dipolar freezing. As the temperature is lowered, the D-Q coupling increases, with the result that the elastic probe of torsion pendulum can see the dipolar freezing process which occurs at lower temperature than quadrupolar freezing. Hence there are two loss peaks in the pendulum measurement.²⁹

The majority of CN dipoles are frozen at temperature ~30 K. However there are some localized

regions where thermally excited or tunneling CN^- dipole , reorientation may be available at T<30 K. We have carefully examined tan δ of the sample in the range of $1.2K \le T \le 30K$ and found no sign of another dielectric loss peak; however, as shown in Fig. 5.2, the low temperature wing of the loss peak centered at ~30 K for 10 KHz is slightly higher than the high temperature wing. This may be caused by the temperature independent contribution of CN^- tunneling motion.

In summary, Brillouin scattering revealed only one relaxation process which may be explained as a result of the overlapping of α and β processes in the gigahertz range. Dielectric measurements show no evidence of the quadrupolar freezing, which was explained due to the weak D-Q coupling at quadrupolar freezing temperature. Asymmetry of the dielectric loss peak indicates the occurrence of CN⁻ reorientation by tunneling at low temperatures.

CHAPTER 6

Low Temperature Relaxation in (KBr)0.5 (KCN)0.5

6.1 Introduction

The low temperature thermal properties of pure dielectric crystals are determined by long wavelength phonons of wavelength ~100 nm at 1.0 K.⁹⁵ For such phonons both a crystal and an amorphous solid appear as an elastic continuum. One may expect that the Debye T³ law for specific heat and thermal conductivity can be applied to both crystalline and amorphous states. However amorphous solids behave in a very different way. As first discovered by Zeller and Pohl,⁹⁶ the low temperature specific heat is proportional to T and thermal conductivity to T². These anomaties are universal and independent of the chemical composition and the purity of the amorphous solids.

To explain these effects, a tunneling state model was proposed by Anderson⁹⁷ et al. and independently by Phillips⁹⁸. They suggested that a certain number of atoms in a glass may have two equilibrium positions corresponding to the two minima of an asymmetric double-well potential as shown in Fig. 6.1 Quantum mechanical tunneling of the low

excitation entity from one of the well minima to the other through the barrier separating them results in two closely spaced energy levels: a two-level system. Distribution of well asymmetry (Δ) and barrier height (V_0) results in a broad range of energy splitting E between the two levels. The thermal properties of the glass can then be determined by the localized two-level systems. Following this model,^{97,98} the specific heat (C) and the thermal conductivity (K) are given by²⁰

C =	• C ₁ T +	(C _n +	⊦ C _a)T ³	(6.1)
	T	U U	31	(/

vith	C ₁ =	$(\pi^2/12)$	k ² Pl	n (4t/τ _{min}),	(6.2)
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and
$$K = (k_B^3 \rho / 6\pi \hbar^2) \sum_i (v_i / P \gamma_i^2) T^2$$
 (6.3)

where P is the density of the two level states, τ_{\min} the minimum allowable relaxation time of the tunneling center, ρ the density of the sample, v_1 the velocity of the acoustic phonon mode i, and v_1 the coupling constant of the tunneling states to the phonon i. The linear term C_1T varies logarithmically with time and the $(C_D+C_3)T$ term is mostly due to the Debye phonon contribution.

These theoretical results can be used to describe '' the experimental data (for reviews, see Ref. 99 and 100). However, there is no satisfactory theory to explain the 't physical origin of such tunneling states. This disadvantage has hindered a detailed understanding of



Fig. 6.1 Asymmetric double well potential with asymmetry Δ , barrier height V_0 , and well separation 2d. $-(\hat{})$

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.amorphous solids.

Recently, $(\text{KBr})_{1-x}(\text{KCN})_x$ were found to exhibit low temperature thermal properties similar to those found in glasses. Measurements on the specific heat^{21,22}, the thermal conductivity^{21,22}, the dielectric constant²², and the ultrasound absorbtion and dispersion¹⁶ have revealed that in $(\text{KBr})_{1-x}(\text{KCN})_x$ with $0.2 \le x \le 0.50$, low-energy excitations are present, characterised by a broad spectrum in energy and relaxation time. The theoretical studies³⁸ have given rise to speculation that the frozen-in dipoles, capable of reorienting by 180° flips, are the tunneling entities that cause the universal glass properties of $(\text{KBr})_{1-x}(\text{KCN})_x$.

In the present work, the relaxation effects in $(KBr)_{0.5}(KCN_{0.5})$ have been studied, using different thermal treatments on the sample, in the temperature range from 0.1 to 1 K. For both quenched and annealed samples the specific heat data are the same and agree with reported results. However, the heat drift results are different for samples with different thermal histories. In addition, the time decay of temperature after applying a thermal pulse has been analysed, and was found to follow a stretched exponential form.

6.2 Experimental

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A 3 He- 4 He dilution refrigerator (Oxford Instrument Ltd.) was used for producing low temperature (0.1-1.2 K) in this experiment.

A copper tray used to hold the sample was mounted in a frame using nylon lines which were loaded with springs to eliminate vibrations. The frame was suspended below the mixing chamber. A mechanical heat switch was used to control the cooling process. If the switch is on, the mixing chamber will thermally contact a gold-plated copper attached to the tray. The operation of the switch should be gentle so that heat generated in switching was minimized.

Three carbon resistance thermometers were located in the mixing chamber, still, and cold plate respectively to monitor changes of temperature. The temperature of the sample was measured by a germanium thermometer which was calibrated previously.¹⁰¹ Each thermometer was connected in series with a standard resistor and a source of constant current. The voltage drop across the thermometer was measured with current flowing in both direct and reverse directions. The average potential thus obtained eliminated thermal emf's. The driving current was adjusted to satisfy requirements for the minimum thermal heat dissipation and maximum measurement sensitivity.

The heating element was a maganium wire (~100 Ω) which wound the sample tray. By measuring the voltage drop across the wire and its resistance, we can accurately know the heat supplied. All electrical leads were well anchored to the thermal sink before reaching the experimental space. The high vacuum ($<10^{-6}$ mm H_g) was maintained around the sample throughout the experiment so that the heat loss from its surface due to gaseous conduction or convection was negligible. At very low temperatures (<1 K), the thermal radiation which is proportional to T⁴ was insignificant.

The entire system was mounted on heavy concrete blocks on a basement floor and pumping lines were tightly secured in order to reduce spurious heating from mechanical vibrations. The whole system was built and tested by Dr. Morrison.

Specific reat capacity was measured by the heat pulse technique.¹⁰² After a known quantity of energy was applied to the sample, temperature drift versus time was recorded. The drift was contributed by the relaxational effect in the sample and a very small heat leakage due to incomplete adiabaticity. The initial and final temperatures of the sample were obtained from extrapolation of temperature to the mid-point of the heating period which lasted 60 seconds. Hence the specific heat capacity (C) and heat drift (Q) can be easily obtained by equations

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 $C = \frac{\Delta E}{m\Delta T}$

 $\dot{Q} = C \frac{T_2 - T}{t_2 - t}$

and

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where ΔE is the energy supplied, which results in a temperature jump ΔT of the sample. In is the mass of the sample, and T_2-T_1 is the temperature change in the time period of t_2-t_1 , after a heat pulse is applied. The total heat capacity of tray and sample, and the heat capacity of the tray were measured in separate operations. The difference was the heat capacity of the sample. The heat drift measurements were also carried out with and without the sample in place.

A $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ single crystal of weight 5.935 g and thickness (h) ~1.20 cm and cross-section (S) ~2.27 cm² was used. The flat cleavage plane of the sample was in thermal contact with the surface of the copper tray via a thin film of silicon grease. The time (Δ t) which is taken for uniform distribution of heat in the sample can be calculated using the relation

$$\Delta t = \frac{mC}{K} \cdot \frac{h}{S}$$
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where m is the mass, C the specific heat and K the thermal conductivity. At 0.4 K, Δt for this sample is about 0.02

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second. The CN concentrations were confirmed by standard chemical analysis with an error of 3%.

6.3 Results and Discussion 6.3.1 Specific heat

In the procedure employed, the system was cooled to liquid nitrogen temperature over 5 days and then to liquid helium temperature over 5 hours. From 1.2 K to 0.1 K, cooling took about 3 hours. If a measurement was immediately carried out at 0.1 K, the sample was referred to as the quenched sample; if it stayed at 0.1 K about 4 hours before the measurement started, the sample was referred to as the annealed one.

Fig. 6.2 shows the specific heat (C) of the sample plotted as C/T versus T^2 . The open circles and stars represent the annealed and quenched samples respectively. A The difference between these two sets of data are insignificant and are within the experimental accuracy of about 5%.

As is the case for structural glasses, the data are better described by the equation (6.1)

 $C = C_{1}T + (C_{3} + C_{D})T^{3}.$

The best fit in Fig. 6.2 denoted by a solid line yields $C_1 = 17.8 \text{ erg/gK}^2$ and $(C_3 + C_D) = 188 \text{ erg/gK}^4$. The magnitude of the linear term C_1 is twice as large as the reported value





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of $C_1 = 9.5 \text{ erg/gK}^2$.²⁰ The difference may be mainly due to two factors. Firstly, C_1 is logarithmically dependent on measuring time: our time scale (~300 sec) is much larger than reported one (~10 sec).²⁰ Secondly, the value of C_1 is impurity dependent and thus sensitive to the small NCO content of the sample, which may be different for samples from different boules.

The value of the C_3+C_D term is in good agreement with the reported one (185 $\operatorname{erg/gK}^4$).²⁰ The C_D term is due to the phonon contribution and can be calculated from the elastic constants of the solid. For $(KBr)_{0.5}(KCN)_{0.5}$, $C_D=196 \operatorname{erg/gK}^4$,²⁰ therefore the anomalous C_3 term (~-10 $\operatorname{erg/gK}^4$) which usually appears in glasses is absent within experimental accuracy for the X=0.5 sample. However, it is present in samples with lower cyanide concentration.²⁰ The same data in Fig. 6.2 are shown in Fig. 6.3 where the specific heat C has been divided by T³ to emphasize departure from T³ Debye behavior (contributed by the thermal phonons at low temperatures). The Debye term is shown by the dashed line.

From our measurements we clearly confirmed the previous reports, i.e., there is a linear anomaly in specific heat in $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$. This property is identical to that of amorphous solids. The physical nature of the low energy excitations in $(\text{KBr})_{1-x}(\text{KCN})_x$ has been briefly discussed in Chapter 1 and Section 6.1. The

detailed discussions which also include other thermal properties such as thermal conductivity can be found in several excellent papers.^{2,20-24} We thus shift our attention to the thermal drift and temperature-time profile as described in the following two sections.

6.3.2 Heat drift

During the course of the experiments, it was noted that the heat drift between the calorimeter tray and its surrounding was different, depending whether or not the tray carried the sample . The results are summarized in Fig. 6.4. Heat drift data for the tray alone was used as the base, indicated by a dashed line. The heat drift for the annealed sample and the quenched one are represented by open circles and stars respectively. The features in Fig. 6.4 are surprisingly similar to the data for glassy carbon monoxide crystal as shown in Fig. 6.5 after Ref. 103. Wee can explain our results closely following Atake et al.'s argument.¹⁰³ For the quenched sample, as shown in Fig. 6.6, the sample was quickly cooled down from T_1 to T_2 . The configuration at T_{γ} of cyanide dipoles remained approximately the same as at T_1 , denoted by entropy $S^{*}(T_{2})(\tilde{z}S(T_{1}))$. Upon heating the crystal to a temperature T3, cyanide dipoles tend to reach a thermal equilibrium state (i.e. $S^*(T_2) \rightarrow S(T_3)$) by guantum tunneling.





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Fig. 6.6 The schematic diagram of heat treatment of the sample.

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Since $S^*(T_2)^{-}S(T_1)>S(T_3)$, the stabilization process would accompany with it a decrease in entropy from $S^*(T_2)$ to $S(T_3)$, resulting in a "hot" drift from the sample to the sample holder where the thermometer was located.

On the other hand, if the sample was cooled from T_1 to T_2 , where annealing took place, the entropy will decrease from $S^*(T_2)(~S(T_1))$ to $S(T_2)$. Upon heating the annealed crystal to T_3 , entropy increases from $S(T_2)$ to $S(T_3)$, thus absorbing heat from the lattice ("cold" drift). At $T_0~0.9$ K, the crystal reaches the equilibrium faster than the measuring time, resulting in disappearance of the heat drift for both the quenched and annealed sample.

This experiment has shown that the microscopic configurational states of $(KBr)_{0.5}(KCN)_{0.5}$ do not completely freeze even at T<1 K, and the relaxation of the CN⁻ dipoles via quantum tunneling was evident in the heat drift data. Here we should emphasize that the present observation does not entirely exclude other interpretations. Further conclusions cannot be drawn until the experiment is repeated.

6.3.3 Non-exponential relaxation

Mastuo et al.¹⁰⁴ have measured the temperature-time curves in $(KBr)_{0.3}(KCN)_{0.7}$. In their experiments, the sample was quenched from 40 K to T ≤ 27 K, then the

temperature as a function of time was recorded in the time interval 60-20000 seconds. They demonstrated that the T-t relation can be best described by the empirical equation

$$T(t) = A + Bt - Cexp[-(t/\tau)^{\beta}]$$
 (6.7)

where T(t) is the temperature at time t, (A-C) the initial temperature, B the constant drift rate due to heat leakage of the apparatus, τ the average relaxation time and β the Williams-Watts parameter.¹⁰⁵ The negative sign of C corresponds to the exothermic relaxation (i.e. spontaneous heating), which usually accompanies the quenching-process.

Motivated by Matsuo's et al. work, we have analysed our temperature-time profile for (KBr) 0.5 (KCN) 0.5, which was measured after a 60-sec heat pulse was applied. The typical curves denoted by stars at various temperatures were shown in Fig. 6.7-6.9 in semilog plots. The slow temperature decay is clearly evident. In contrast, the same measurement on pure copper showed that the thermal equilibrium time was less than a few seconds. The temperature rise for pure copper is schematically plotted in the inset in Fig. 6.7. Slow temperature decay is not due to the poor thermal conductivity of the (KBr)0.5(KCN)0.5 either. A straightforward calculation in section 6.2 has revealed that the time for heat distributing through the sample with x=0.5 was less than 1 second. We thus conclude that the T-t curves in Fig. 6.7 - 6.9 are the genuine 11

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Fig. 6.7 Semilog plot of temperature of x=0.5 as a function of time after application of a 60-sec heat pulse at a mean temperature $T_m=0.32$ K. The solid curvé is the best stretched exponential fit to the data. The inset schematically shows the T-t profile for pure copper.




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T=0.82K



time at T_m =0.82 K.

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property of the sample.

The solid lines in Fig. 6.7 - 6.9 represent calculations using the equation

$$T(t) = A + C \exp[-(t/\tau)^{\beta}]$$
 (6.8)

which differs from eqn. (6.7) in two ways. Firstly, the linear term in eqn. (6.7) was neglected. This is justified since the heat exchange between the sample and the mixing chamber was very small (the heat switch was off), and had little influence on the present data. Secondly, the positive sign was used for C, which represents the endothermic relaxation (i.e. absorbing the heat). The fitting parameters are listed in table. 6.1. β and τ obtained by Mastuo et al. for the x=0.70 sample are also included for comparison.

Earlier work¹⁰⁶ with this calorimeter has shown that the temperature-time profile as for CH_3D crystals can be fitted by an exponential function (β =1) with a single relaxation time τ ~12 sec. Such a thermal relaxation effect has been attributed to the conversion between the nuclear spin symmetry species¹⁰⁶ at low temperatures.

The present work revealed that the temperature-time curve for $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ at T<1 K can be described by a stretched exponential form with the Williams-Watts parameter β <1.

The stretched exponential form has been widely used

Table 6.1

Parameters for the stretched exponential fits, T(t) = A + Cexp $[-t/\tau)^{\beta}$], to the temperature-time profiles at different temperatures T_m for the x=0.5 sample. Fitting parameters for x=0.7 are also included for comparison

(mode%)	T _m (K)	A(K)	С(К)	τ(s)	β
0.5	0.32	0.3160	0.0200	584	0.54
	0.46	0.4395	0.0450	540	0.5
	0.59	0.5635	0.0678 ·	520	0.5
	0.82	0.7835	0.0955	475	0.6
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0.7	23	_ .	-	6900	0.7
(→ ²⁵	. – ·	-	6000	0.6
· · · /	27	-	л. — .	6000	0.5
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to describe the relaxation behavior in various glasses (for a review, see Ref. 107). Recently, the time-decay of the remnant magnetization in spin glasses was also characterized by the stretched exponential form.¹⁰⁸ Palmer et al.¹⁰⁹ has proposed a hierarchically constrained dynamic model to theoretically justify such a form. The present results for $(KBr)_{0.5}(KCN)_{0.5}$ may be qualitatively explained as follows.

After a heat pulse was added to the sample under an adiabatic condition, the temperature rise ΔT decays with time, as an increasing number of the low energy excitations take up energy from the rest of the sample. If the low energy excitations have the same relaxation time τ , we will see Williams-Watts parameter $\beta=1$. However, in the present case, the low energy excitations consist of CN tunneling The barriers for CN^{-} tunneling have a Gaussian centers. distribution, 38 therefore resulting in a distribution of relaxation times, which are characterized by $\beta < 1.^{107}$ Since the glassy low temperature thermal properties appear to be insensitive to the presence of long-range crystalline orientational order², the relaxation effects observed for both x=0.7 and x=0.5 were caused by the cyanide dipolar process at T<40 K. The orientation of CN dipoles was hindered by the barriers created by CN-CN quadrupolar interactions. At T>1 K, CN diopoles were thermally excited over the barriers, while at T<1 K, CN ions

reorient by tunneling through the same barriers. Therefore the distribution of relaxations should be present in both relaxation curves at T~25 K and at T<1 K, which explains the consistency of β (~0.6) obtained by Mastuo et al. and ourselves. At this time, the temperature dependence of τ

is not yet understood.

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CHAPTER 7

Brillouin Scattering Study of Propylene Glycol

7.1 Background theory

As a liquid is cooled, the rate of any molecular diffusion process necessary to accomplish structural rearrangement becomes increasingly slow. By sufficiently rapid cooling, there will be a temperature, T_g , below which the relaxation time necessary for any structural changes to occur will be much longer than the time scale of a probe of order a few minutes. In this region the liquid is said to become a glass. The kinetics of structural relaxation in liquids and the nature of the glass transition have consistently attracted much attention. For a recent review, see reference 110.

Since glasses are formed from viscous liquids, a better understanding of the glass transition must derive from a detailed study of viscous liquids. A great deal of experimental data have revealed that the temperature dependent structural Telaxation times in most liquids follow the empirical Vogel-Tamman-Fulcher (VTF) equation¹¹¹ given by

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$$
(7.1)

where B, τ_0 and T_0 are experimentally determined parameters. B is related to the activation energy for relaxing molecules, and T_0 represents an experimentally inaccessible state where the relaxation time τ diverges. If $T_0=0$ K, eqn. (7.1) simplifies to an Arrhenius form. There have been some attempts made to theoretically justify the VTF equation, either through the free-volume theories¹¹² or entropy theories.¹¹³ However, there is no universal acceptance of these theories. A critical review can be found in Ref. 114.

Recently, hydrodynamic theories¹¹⁵ have been proposed to explain the kinetics of structural relaxation in liquids near the glass transition. These theories make no specific reference to the microscopic details of the liquid, but rather they start with general compressive hydrodynamic equations. One of the consequences of these theories is that the relaxation time in viscous liquids should follow a scaling law, as

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$$\tau = \tau_0 \left(\frac{T_0}{T - T_0} \right)^{\beta}$$
(7.2)

where τ_0 , T_0 and β are fitting parameters. The theoretical value of index β is about 2.

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These theories have generated extensive interest since they do not depend on the microscopic details of any particular liquid and should apply to all liquids. These theories have been tested on glycerol and propylene glycol (PG) using ultrasonic and frequency-dependent specific heat techniques. 58,116,117 The relaxation data near the glass transition region were found to be equally well fitted by two very different functional forms: the VTF equation and the scaling law. These experiments have been limited to the frequency range below 10^8 Hz for glycerol, and 10^2 Hz for PG. Hence these measurements explored a rather slow / viscous state of the systems.

In the present work, the study of relaxation in PG is extended to high temperatures, using the Brillouin scattering technique which allows us to explore relaxation phenomena in the gigahertz frequency range.

The differential cross section for scattering of light by a liquid is expressed as 45 7

$$\frac{d\sigma}{d\Omega} = \frac{\omega_{i}^{4} V k_{B} T}{16\pi^{2} c^{4}} \left(\beta_{s} \rho^{2} \left(\frac{\partial \chi}{\partial \rho} \right)_{s}^{2} + \frac{T}{\rho C_{p}} \left(\frac{\partial \chi}{\partial T} \right)_{P}^{2} \right)$$
(7.3)

where $\beta_{\rm S}$ is the adiabatic compressibility, ρ is the density, $\omega_{\rm i}$ is frequency of the incident light, V is the scattering volume and $C_{\rm p}$ is the specific heat. The effects of fluctuations in the pressure P and the entropy S on the dielectric susceptibility χ are given by $(\partial \chi / \partial \rho)_{\rm S}$ and

 $(\partial \chi/\partial T)_p$ respectively. The first term in the bracket in eqn. (7.3) is associated with the sound wave modes of the Brillouin doublet corresponding to density fluctuation at constant entropy. The second term in eqn. (7.3) corresponds to nonpropagating entropy (temperature) fluctuations at constant pressure and gives rise to the Rayleigh scattering component.

In this experiment we are only interested in the Brillouin component. The measured Brillouin shift ν and linewidth Γ (FWHM) are related to the sound velocity ν and sound wave absorption coefficient α by the following expressions¹¹⁸

 $\alpha = \frac{\pi\Gamma}{V}$

$$v = \frac{\nu \lambda_{\tilde{0}}}{2n' \sin(\theta/2)}$$
(7.4)

and

where λ_0 is the incident light wavelength, θ the scattering angle and n the index of refraction. The hypersonic absorption and velocity dispersion obtained in Brillouin scattering can thus be used to establish the characteristics of the structural relaxation in PG in the gigahertz frequency range. Combining our light scattering data and specific heat data, we are able to test the VTF equation and the scaling law over twelve decades, which cover both very viscous and very fluid regions of PG.

(7.5)

There are few experimental data for PG in the sub-T_g region, where the very slow relaxation process is not easily accessible to the conventional techniques such as ultrasonic, heat capacity, or dielectric measurements. Realizing that the structural relaxation in the sub-T_g region does not necessarily follow a VTF equation, ^{119,120} we have tried to use time-resolved Brillouin scattering to study this slow relaxation process.

The idea is simple: in the sub- T_g region, it takes from minutes to hours for structural relaxation to reach an equilibrium state and this may have an influence on the Brillouin frequency. Since this relaxation time is comparable to the time for acquisition of a Brillouin spectrum, the change in Brillouin shift with time can be followed. By study of the Brillouin shift versus time. profile, we may establish relaxation behavior in the sub- T_g region.

7.2 Experimental

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Propylene glycol (PG) with 99% assayed purity was purchased from Aldrich Chemical Co.. PG is a good glass former and does not crystallize upon cooling because it has two incompatible stereoisomers that do not fit into each other's crystal lattice.¹²¹

The sample was placed into a cylindrical pyrex cell

and mounted in a continuous flow helium cryostat. Both the sample and the sample cell have poor thermal conductivity. Even at temperature region far above the PG glass transition (T_g ~172 K), after a temperature drop (eg. from 230 K to 200 K), it took about 15 minutes for the sample to reach a thermal equilibrium temperature. In order to increase the heat distribution rate, the glass cell was covered by a thin metal plate with a copper finger inserted into the liquid sample. The metal plate was direct contact with the cold finger of the cryostat. A sheet of indium was placed between the bottom of the cell and the mount to minimize thermal resistance.

The cooling rate was adjusted by varying the helium flow valve. For a fully opened valve, the rate of 30 K/min could be obtained. Since a very fast cooling rate would crack the sample cell, the maximum quenching rate was set at about 10 K/min in this measurement. Temperature was varied from 4.2 K to 330 K by adjusting both the flow rate of helium gas and a registance heater.

The time-resolwed Brillouin measurement requires very short collection time. With the advantage of the computer data processing, the spectral profile can be stored on a hard disk in a matter of seconds. Due to the relatively strong Brillouin scattering intensity of PG, we can obtain the spectrum with good signal-to-noise ratio in 2-minute collecting time.

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The scattering experiments were carried out using the first etalon of the tandem Fabry-Perot interferometer in two pass with 90° scattering geometry. The frequency of the longitudinal acoustic sound wave in PG was measured as a function of temperature. The magnitude of the frequency was the average of the Stokes and anti-Stokes frequency values. The Brillouin width which represents the attenuation of the sound wave was determined by fitting the Brillouin'peak using the convolution of a Lorentzian shape phonon profile with an instrumental function (for details, see section 3.3.1).

7.3 Results and discussion

The frequency (stars) and the full width at half maximum (FWHM) (open circles) of the longitudinal acoustic sound wave in PG are shown in Fig. 7.1 as a function of temperature. The slight change in the slope of frequency versus temperature at around 172 K marks the occurrence of the glass transition. This value agrees with the glass transition temperature, T_g , determined by the differential scanning calorimetry measurement.¹²¹ Above T_g , the frequency of the sound wave decreases, while the linewidth increases. At ~310° K the linewidth reaches a maximum, indicating the maximum attenuation of the sound wave due to the match between the sound frequency and the viscoelastic

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Fig. 7.1 The temperature dependence of the frequency (*) and linewidth (0) of the longitudinal acoustic phonon in PG. The arrow marks the glass transition temperature $T_g=172$ K. solid lines are guides for the eye. The dashed line represents v_0 .



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structural relaxation rate. These general features are very similar to those observed previously in other viscous liquids.¹²²

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The measured Brillouin shift γ and linewidth Γ (FWHM) are related to the sound velocity v and absorption coefficient α by eqns. (7.4) and (7.5) respectively. For a single relaxation time, the frequency dependent velocity and absorption of the longitudinal sound wave are further given by^{118,123}

$$v^{2} = v_{0}^{2} + (v_{\infty}^{2} - v_{0}^{2}) - \frac{\omega^{2}\tau^{2}}{1 + \omega^{2}\tau^{2}}$$
(7.6)
and $\alpha = \frac{1}{2v^{3}} \frac{(v_{\infty}^{2} - v_{0}^{2})\omega^{2}\tau^{2}}{1 + \omega^{2}\tau^{2}}$ (7.7)

where τ is the relaxation time of the liquid, v_0 and v_{∞} are the sound velocity at the low and high frequency limits respectively.

Combining eqns. (7.6) and (7.7), we obtain the longitudinal relaxation rate

$$f = \frac{1}{\tau} = \frac{2\alpha v^3}{v^2 - v_0^2}$$
(7.8)

which makes it possible to calculate τ from two independent measurements: the Brillouin frequency and linewidth.

The low frequency velocity v_0 is usually obtained by

measuring the sound frequency (ν) at very high temperatures where the ν versus T relation in the sample levels off. However, due to the limitation of the apparatus, the temperature in this experiment could not increase high ν enough to reach such a region. Alternatively we obtain the temperature dependence of ν_0 by linearly extrapolating the calculated value of ν_0 =1418 m/s at the maximum linewidth (T_m =310 K) using eqn. $2\pi\nu_m\tau_m$ =1 and eqn. (7.8), and the value of ν_0 =1650 m/s measured at 235 K by the low frequency ultrasonic experiment.¹²⁴ These two data are then converted to sound frequencies with eqn. (7.4) and are shown in Fig. 7.1 with the plus sign for the calculated value and the solid circle for the ultrasonic one. The dashed line represents the linear extrapolation.

Following Jeong's et al. argument⁵⁸, the hypersonic measurements study the adiabatic relaxation process, while the low frequency specific heat measurements probe the isothermal process.

The relation between the adiabatic and isothermal relaxation rate (f_S and f_T , respectively) is given by ^{58,117}

$$f_{T} = \frac{c_{p\infty}}{c_{p0}} f_{S}$$
(7.9)

where C_{PO} is the equilibrium specific heat and C_{Po} includes all the degrees of freedom that equilibrate very quickly. Furthermore, the relaxation rate obtained with eqn. (7.8)

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is at constant volume (V) (i.e. f_V).¹²³ However, specific heat data yields the relaxation rate at constant pressure (i.e. f_p). Their relation is given by¹²³

$$f_{V} = \frac{k_{\infty}}{k_{0}} f_{P}.$$
 (7.10)

where k_{∞} and k_0 are the compressional modulus at high and low frequency limits, respectively. Thus the overall conversion should be carried out by

$$f_{T,P} = \frac{C_{P\infty}}{C_{P0}} \frac{k_0}{k_{\infty}} f_{S,V}$$
 (7.11)

where $f_{S,V}$ is the calculated rate via eqn. (7.8) from measured Brillouin scattering data, and $f_{T,P}$ can be used tp directly compare with the relaxation rate obtained from the specific heat data. For PG, $C_{p\omega}/C_{P0}^{-0.5}$,¹¹⁵ and $k_0/k_{\omega}^{-}(v_0/v_{\omega})^{2}$.25 obtained from Fig. 7.1. The final values of $f_{T,P}$ are plotted against 1/T as shown in Fig. 7.2 in half-filled circles. The relaxation rates measured by frequency dependent specific heat experiments are also included in Fig. 7.2 (open circles) for comparison.

The solid line is the best fit for both Brillouin scattering and specific heat data using a VTF equation

$$\overrightarrow{f}_{T,P} = 10^{\alpha} \exp\left(-\frac{A}{T-T_0}\right)$$
(7.12)

Fig. 7.2 The logarithm of relaxation rate is plotted against 1/T. Symbol 0 represents heat-capacity data¹¹⁷ and 0 our Brillouin scattering data. The solid line is VTF fitting, and the dashed line is the scaling law fitting after Ref. 117. The present scaling law fitting is represented by the dotted line.

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with $\alpha=14$, $T_0=119$ K and A=1900 K. These values are in good agreement with those previously reported, ¹¹⁷ viz., $\alpha=13.8\pm0.4$, $T_0=114\pm7$ K and $A=2020\pm130$ K. The dashed line is the fitted curve of the "scaling law (after Ref. 117):

$$f_{T,P} = 10^{\alpha} \left(\frac{T - T_0}{T_0} \right)^{\beta}$$
(7.13)

where $\alpha = 10.3 \pm 0.1$, $T_0 = 148 \pm 1$ K and $\beta = 14.6 \pm 0.6$.

As evident from Fig. 7.2, the relaxation rate for PG can be well fitted by both the VTF equation and the scaling law near the glass transition region. However, at temperatures far away from T_g , the system is best described by the VTF equation.

An attempt was made to fit all of the data using the scaling law with three free parameters, α , T_0 and β in eqn. (7.13). The results are shown in Fig. 7.2 in the dotted line with α =9.78, T_0 =158 K and β =10.5. A good fit at both high and low temperature data is obtained. However, the values of the parameters exceed the error limits set by Ref. 117. Summary of these fitting parameters is listed in table 7.1.

The scaling exponent for PG, our value of β =10.5 and Birge's value of β =14.6, is considerably larger than the theoretical value of $\beta^2 2$.¹¹⁵ At present we can not explain such discrepancy. The value of T₀(~158 K) derived from the scaling faw fitting is much higher than T₀ (~119

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Table 7.1

Parameters for the VTF fits, $f=10^{\alpha} \exp[-A/(T-T_0)]$, and for the scaling law fits, $f=10^{\alpha}[(T-T_0/T_0]^{\beta}$, to both Brillouin and specific heat data (Bril. + S.H.) for propylene glycol. Parameters From Ref. 177 are also included for comparison

VTF	range	α	T _O (K)	A(K)
s.H. ¹¹⁷	170 K - 200 K	13.8±0.4	114±7	2020±130
Bril.+S.H.	170 K - 340 K	14.0±0.1	119±2	1900±10
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Scaling Law	range	α	т _о (к)	B
S.H. ¹¹⁷	170 к - 200	K 10.3 ±0.1	148±1	/ 14.6±0.6
Bril.+S.H.	170 K - 340	K 9.78±0.1	158±1	10.5±0.2 '

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K) from the VTF fitting in PG. Such inequality was also observed in the glycerol.⁵⁸ However, there is no theory to show the relation between these two T_0 's.

A liquid can be usually characterized by a single relaxation time at high temperatures where each molecule sees the same environment as its neighbor.¹¹⁸ As temperature decreases, random clusters of molecules in the liquid are created. Different regions in the liquid may possess different activation energies and therefore have different relaxation times associated with each. Therefore our Brillouin relaxation data are limited to a narrow temperature range. At these high temperatures we may use a single relaxation approximation with eqn. (7.8). For lower temperatures, Brillouin data deviated from the present pattern. More complex formulae which take into account the distribution of relaxation rates of the liquid should be employed.

Brillouin light scattering experiments were also performed in the sub-T_g region, where the supercooled liquid is arrested in non-equilibrium states. Recovery time to move to the equilibrium state is dependent on how far T falls below Tg^{120} .

Fig. 7.3 shows the Brillouin shift in PG as function of time various temperatures. Here all data were taken after a temperature drop from 30 K above T_g to the assigned T. The dropping rate was about 10 K/min.



Fig. 7.3 The Brillouin frequency versus time at $\operatorname{sub-T}_g$ region for PG. The data was taken after cooling down (10 K/min) from 30 K>T to the temperatures indicated.

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However, there was no change in Brillouin frequency as evident in Fig. 7.3. This may be explained as follows.,

The longitudinal sound velocity (v) is related to the elastic constant C in the sample with density ρ by¹¹⁸ C = ρv^2 (7.14)

Combining eqns. (7.4) and (7.14), the phonon frequency (ν) is given by

$$\nu \propto \frac{n\sqrt{C}}{\sqrt{\rho}}$$
 (7.15)

It is known that the refractive index n, ¹²⁵ elastic constant C¹²⁶, and density ρ^{127} of supercooled liquids all increase with time at T<T_g upon quickly cooling from T>T_g to T<Tg, due to the slow structural relaxation.¹²⁰ If the increase of n/C is comparable to the increase of $\sqrt{\rho}$, the Brillouin frequency will show no change. This may be the case of propylene glycol.

Angell¹²⁸ has classified liquids into a "strong" type at one extreme and a "fragile" type at the other. The strong liquids have an Arrhenius relaxation behavior, like ${\rm SiO}_2$, while the "fragile" liquids follow a VTF law, like PG. The time-resolved BFillouin scattering technique may be used to investigate relaxation behavior in "strong" liquids at sub-T_g region, where the change of $n\sqrt{C}$ should be greater than the change of $\sqrt{\rho}$ as a function of time.

In summary, the relaxation rate of PG in the

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gigahertz range was found in good agreement with the low frequency specific heat data, following the same VTF relation_over 12 decades. The scaling law calculation yields fitting parameters which are somewhat different than those reported. The scaling exponent β for both different sets of fitting is higher than the theoretical value. The time-resolved Brillouin scattering was shown as a promising technique to investigate slow relaxation behavior in supercooled liquids.

V

CHAPTER 8

10

Summary and Conclusion

This thesis has investigated two disordered systems: $(KBr)_{1-x}(KCN)_x$ mixed crystals and the propylene glycol viscous liquid. The important results of this study are summarized as follows.

1. Our Brillouin light scattering measurements on

 $(\text{KBr})_{1-x}(\text{KCN})_x$ for X=0.35 and 0.5 have revealed that the T_{2g} acoustic phonon frequency and linewidth exhibit a minimum and a maximum around the quadrupolar freezing temperature respectively, and the Brillouin intensity shows an anomalous maximum at T_f . All these experimental results for the Brillouin spectra can be semi-quantitatively explained by Michel's theory which considers that the formation of the quadrupolar glass is due to the competing effect between the translation-rotation coupling. The reorientational frequency of CN⁻ quadrupoles was calculated from the acoustic phonon data and found to follow an Arrhenius law with an activation energy of 1230 K for x=0.5 and 849 K for x=0.35. The

elastooptic constant P_{44} of $(KBr)_{1-x}(KCN)_x$ was also determined by the Brillouin intensity measurements.

- 2. We have examined the quasielastic scattering in $(KBr)_{1-x}(KCN)_x$ using the high resolution tandem multipass Fabry-Perot interferometer. The width of this central peak versus temperature has an Arrhenius relation with a hindering barrier ~612 K for x=0.5, and ~562 K for x=0.35. The peak intensity is proportional to $1/T^2$ near T_f and agrees with Michel's prediction. We attribute this central peak to the dynamic relaxation process of the cyanide dipolar reorientation.
- 3. Under a uniaxial stress, the selection rules for Brillouin scattering in $(KBr)_{1-x}(KCN)_x$ were broken. This effect is explained by a stress-induced partial cyanide quadrupole alignment, which causes a weak birefringence effect and significantly influences the polarization state of the Brillouin scattering component.
- 4. Only one dielectric loss peak at ~30 K was found in the dielectric measurement on $(KBr)_{0.5}(KCN)_{0.5}$ in the temperature range from 1.2 K to 294 K. There was no indication of another loss peak due to quadrupolar freezing at ~80 K. We thus suggest that the dipole-quadrupole coupling is temperature dependent: at a high temperature, such as 80 K, this coupling effect can be neglected; at low T, it becomes significant and can be

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detected by the pendulum measurement.

- 5. The specific heat of $(KBr)_{0.5}(KCN)_{0.5}$ was measured below 1 K and the results are in good agreement with previous reports. In addition, we found that the heat drift was different for the sample which experienced different thermal treatment. We attribute this effect to the cyanide relaxation by tunneling. We also found that the temperature-time profile after a thermal pulse follows a stretched exponential form, which indicates there is a distribution of CN^- relaxation times below 1 K.
- 6. The structural relaxation rate in propylene glycol in the gigahertz range was found to agree with the low frequency specific heat data, following the same VTF equation over 12 decades. The scaling law calculation, however, yields fitting parameters which are different from those reported. The time-resolved Brillouin scattering was shown as a promising technique to investigate very slow relaxation phenomena at temperatures below T_{α} .

Our studies show that Michel's theory is capable of explaining the basic experimental features of the quadrupolar freezing in $(\text{KBr})_{1-x}(\text{KCN})_x$. Naturally we may wonder whether the same techniques and approaches can be used to study other mixed crystals. The most promising candidates are $(\text{RbCN})_{1-x}(\text{KCN})_x$ and $(\text{NaCN})_{1-x}(\text{KCN})_x$.¹²⁹⁻¹³²

4

The random strain fields associated with two alkali ions of dissimilar size for $(NaCN)_{1-x}(KCN)_x$ are larger than those for $(RbCN)_{1-x}(KCN)_x$, since the ratio of radius r(K)/r(Na)=1.24 is larger than r(Rb)/r(K)=1.07. In fact,¹²⁹ $(NaCN)_{1-x}(KCN)_x$ form an orientational glass state over a wide CN^- equcentration range (0.15 < x < 0.9). In contrast, $(RbCN)_{1-x}(KCN)_x$ has no glass phase at all for any $CN^$ concentration. These two systems have barely been studied and provide a new opportunity for future experimental and theoretical investigation.

From this thesis, we have increased our overall understanding of the orientational glass. Although we have not been able to generalize our results to other glasses, we may consider other glasses as consisting of random elastic quadrupoles.¹³³ This new glass model, along with the random network model of the amorphous semiconductors, the random close packing model of the metal glass and the random coil model of polymers,¹ may stimulate more detailed and realistic approaches to disordered materials in general.

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