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NEUTRON SCATTERING STUDIES OF ANION DISORDER IN FLUORITES AT HIGH TEMPERATURES

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Abstract. — Certain classes of ionic solids exhibit ionic conductivities, at temperatures appreciably below the melting point, which are comparable with those found in liquid electrolytes (these compounds are sometimes referred to as fast-ion conductors or superionics). Fluorites represent one such class which possess a relatively simple structure. In these materials the high ionic conductivity is due to disorder in the anion sublattice. A rather diffuse specific heat anomaly related to the disorder occurs at a temperature $T_e$. The aim of the present study is to provide information about the nature of this dynamic disorder using neutron-scattering techniques. Attention has been focussed on PbF$_2$, SrCl$_2$ and BaF$_2$ which have values of $T_e$ ~ 830, 1 000 and 1235 K respectively. Certain Bragg reflections show marked variation with temperature in the vicinity of $T_e$ and anomalies have also been observed in the energies, widths and intensities of individual phonons. The origins of these anomalies are discussed.

Résumé. — Quelques classes de solides ioniques présentent des conductivités ioniques aux températures sensiblement au-dessous du point de fusion qui sont comparables à celles qui se trouvent dans les électrolytes liquides (ces composés s'appellent parfois fast-ion conductors ou superionics). Les fluorites représentent une telle classe qui possède une structure relativement simple. Dans ces matériaux la haute conductivité ionique est due au désordre du sous-réseau des anions. Une anomalie assez diffusée de la chaleur spécifique ayant rapport au désordre se produit à une température $T_e$. Le but de cette étude est de fournir des informations au sujet de ce désordre dynamique en utilisant les méthodes de diffusion neutronique. Nous avons concentré nos efforts sur PbF$_2$, SrCl$_2$ et BaF$_2$, lesquels ont respectivement des valeurs de $T_e$ d'environ 830, 1 000 et 1235 K. Quelques réflexions de Bragg présentent de grandes variations aux températures voisines de $T_e$ et on a aussi observé les anomalies des énergies, des largeurs et des intensités des phonons individuels. On discute les origines de ces anomalies.

1. Introduction. — Certain ionic solids exhibit anomalously high ionic conductivities at temperatures well below their melting points $T_m$ and this has led to applications in high-energy-density batteries, fuel cells and gas monitors [1]. The transition to the highly-conducting phase may be sharp or diffuse. In AgI, for example, there is a first-order change with increasing temperature from a hexagonal to a cubic structure at $T_c = 420$ K. The conductivity increases by more than three orders of magnitude at $T_c$ and the change of entropy is comparable to the entropy of fusion. In the high-temperature phase the b. c. c. iodine lattice provides a large number of equivalent or nearly equivalent sites for the Ag$^+$ ions, and it is intercell and intra-cell motion between these sites which is responsible for ionic conduction.

In contrast, some fluorites exhibit a diffuse structural transition at high temperatures in which the ionic conductivity varies smoothly. For example, the electrical conductivity of PbF$_2$ increases approximately exponentially with temperature up to a value of $\sim 10^2 \Omega^{-1} \text{m}^{-1}$ at about 800 K and thereafter does not change appreciably with temperature up to $T_m = 1 120$ K [3]. Similar results are found for SrCl$_2$. The conductivity increasing rapidly up to 100 K, and then less rapidly between 1 000 K and the meeting point $T_m = 1 146$ K [3]. Corresponding specific heat anomalies have also been observed in some fluorites. In SrCl$_2$ a specific heat anomaly occurs at $\sim 1 000$ K and the associated entropy appears to be comparable with the entropy of fusion [4]. The heat capacity of PbF$_2$ increases rapidly between 625 and 700 K with an entropy increase of 16.5 J K$^{-1}$ mole$^{-1}$ [5]; this may be compared with the entropy of fusion, 16.4 J K$^{-1}$ mole$^{-1}$ [6], indicating a high degree of disorder below the melting point. In BaF$_2$ which has $T_m = 1 553$ K there is a specific heat anomaly at $\sim 1 235$ K [7]. The above data suggest a rather diffuse transition to a disordered state at $T_c \approx 830$ K, 1 000 K and 1 235 K in PbF$_2$, SrCl$_2$ and BaF$_2$ respectively.

Anion Frenkel pairs are the principal source of...
disorder in fluorite crystals [8]. The fluorite structure consists of cubes of eight anions with cations at every other body centre. Neutron diffraction studies at high temperatures (but below $T_c$) have shown that the anions vibrate anisotropically in $<111>$ directions towards the empty cube-centre sites [9]. There are four such interstitial sites for each eight anions. The relative simplicity of this structure suggests that dynamic disorder in these crystals should be more amenable to investigation than in other materials exhibiting high ionic conductivity.

A combination of experimental approaches, including specific heat, electrical conductivity, dielectric loss and X-rays measurements is essential for the study of disordered systems. In addition, both light scattering and neutron scattering can make important contributions. Brillouin and Raman scattering have been used to investigate changes of elastic constants and of phonon spectra in fluorites near $T_c$ [10]. Neutron scattering measurements, elastic, quasielastic and inelastic have a unique role to play. An investigation of the temperature dependence of diffraction peaks is of major importance since it provides information about ion configurations in a disordered crystal. Measurements of quasielastic scattering give information about the frequency spread of ionic motion both within unit cells and between unit cells [11]. The temperature dependence of individual phonon frequencies and linewidths and also the single-phonon density of states provide additional useful information about the nature of the disorder.

We shall be concerned here primarily with elastic and inelastic neutron scattering studies of PbF$_2$, SrCl$_2$ and BaF$_2$ at temperatures up to $\sim$ 1 000 K.

2. Experimental results. — We first describe results of neutron diffraction measurements on PbF$_2$ and SrCl$_2$ powder samples, made using the Harwell Panda diffractometer with incident neutrons of wavelength 1.3 Å. The samples were sealed in vacuo by electron-beam welding into platinum tubes; the use of platinum was dictated by the corrosive nature of PbF$_2$ and SrCl$_2$ at high temperatures. We have measured integrated intensities of the first 14 to 18 Bragg peaks at temperatures below and above $T_c$; up to 1 020 K in PbF$_2$ and 1 070 K in SrCl$_2$. These data were analysed initially in the context of an assumed defect-free fluorite lattice with harmonic oscillations of the Pb$^{2+}$ ions and anharmonic oscillations of the F$^-$ ions. We find (see Fig. 1) that in PbF$_2$ the fitted temperature factor for fluorine, $B_F$ (defined in a term $\exp(-B_F \sin^2 \theta/\lambda^2)$ multiplying the contribution to the structure factor of ion j), shows a dramatically larger increase with temperature than the lead temperature factor, $B_{Pb}$. This indicates that the fluorine ions undergo very large amplitude vibrations at high temperatures. However, it should be noted that the $R$-factor describing the goodness of fit increases from 5% at low temperature to 10% at high temperatures. The fitted fluorine anharmonic factor, $\beta_{F\text{anh}}$, related to $\beta$ [12] by $\beta_{F\text{anh}} = -(B_B/4\pi a_0)^2/\lambda^2$ is observed to increase with temperature. It implies that the high-temperature state involves highly anisotropic fluorine vibrations favouring the $<111>$ directions, or alternatively that there is some average displacement in these directions. Our results on PbF$_2$ and similar results which we find for SrCl$_2$ correspond to anharmonic effects observed previously in CaF$_2$ at temperatures below the disordered regime ($T < T_c$). A similar investigation of BaF$_2$ has recently been reported by Thomas [13]. We have extended the data analysis by fitting the data to models involving partial occupation by the fluorine ions of the interstitial sites. When the data are analysed in terms of partial occupation of the $(\frac{1}{2} \frac{1}{2} \frac{1}{2}) a_0$ interstitial site, however, we find very little improvement in the large high-temperature $R$-factors suggesting that a simple model of interstitial disorder is not adequate. An alternative approach has been used by Axe et al. [14] in which the data is Fourier transformed directly to give the nuclear density distribution. However errors due to the finite termination of the series occur and the uniqueness of the transformation is uncertain. It appears that more accurate neutron measurements of powder samples out to larger values of momentum transfer Q, or, perhaps single crystal diffraction, are required to provide unambiguous evidence for the nature and the extent of the high-temperature disorder.

**Fig. 1.** Temperature factors for Pb and F ions in PbF$_2$ and anharmonic factor $\beta_{F\text{anh}}$.  

![Temperature factors for Pb and F ions in PbF$_2$ and anharmonic factor $\beta_{F\text{anh}}$.](image-url)
The lattice dilation is of interest since a possible mechanism for a transition to a disordered state involves interaction between defects via the strain field which they induce [15]. However, our measurements of the lattice parameter of PbF$_2$ and SrCl$_2$ as a function of temperature do not show dramatic changes near $T_c$ although in SrCl$_2$, a change of slope is apparent (Fig. 2) (see also Shand et al. [16]). Although there is experimental evidence to show that fluorine interstitials cause an increase in lattice parameters in CaF$_2$ [17] the effect of the fluorine vacancy has not been established. It is possible that generation of a Frenkel pair does not produce an appreciable net effect on the lattice parameter of the crystals investigated by us.

The inelastic neutron scattering work on the fluorites was carried out on triple-axis spectrometers at Harwell and at the Institut Laue-Langevin using a constant-momentum-transfer mode, with incident neutron wavelengths in the range 0.9-2.3 Å. As a preliminary to high-temperature experiments we have measured the low-temperature phonon dispersion relations for PbF$_2$ and have fitted the results to a shell model (1). Data for the low-temperature lattice dynamics of SrCl$_2$ [18] and BaF$_2$ [19] are already available in the literature.

Typical of the high-temperature effects which we observe in the optic modes are those shown for the $\Gamma_{25}$ mode in SrCl$_2$ (see Fig. 3). This is the Raman active mode; it consists of antiphase vibration of the chlorine sublattices with the strontium sublattice static. At room temperature we find a well-defined mode of width about 0.9 THz (not corrected for resolution broadening). As

![Graph](image1)

![Graph](image2)

![Graph](image3)

**Fig. 2.** - Lattice parameter variation with temperature for PbF$_2$ and SrCl$_2$.

**Fig. 3.** - $\Gamma_{25}$ optic mode in SrCl$_2$.

(1) Dickens, M. H. and Hutchings, M. T., to be published.
the temperature is increased to 230 °C and 440 °C, the width is seen to increase to about 2.0 THz; this represents predominantly the intrinsic width of an increasingly anharmonic optic-phonon group. The phonon group is clearly also becoming less intense and is shifting to lower energy. As the temperature is raised through \( T_c \), the phonon becomes unobservable as a discrete mode. We have observed similar effects in \( \text{PbF}_2 \) occurring at lower temperatures corresponding to the lower value of \( T_c \) in \( \text{PbF}_2 \). The intensity appears to be transferred progressively into a low energy-transfer response which may be partially attributable to quasi-elastic scattering from the mobile halogen atoms. This effect has been studied in greater detail in the case of AgI where neutron time-of-flight measurements have detected quasielastic effects implying a local random motion of Ag\(^+\) ions and also a translational motion of the jump-diffusion type [11].

The acoustic modes also show extreme anharmonicity at temperatures approaching the order-disorder transition. Figure 4 shows typical acoustic phonon widths in \( \text{PbF}_2 \) as a function of temperature. We see an anomalous increase in the phonon width near \( T_c \).

The acoustic-mode energies, defined by the centre of the measured phonon groups, show pronounced renormalization at high temperatures. Figure 5 shows energies of transverse and longitudinal modes propagating in the \([0 \ 0 \ 0], [\xi \ \xi \ 0] \), and \([\xi \ \xi \ \zeta] \) directions. For comparison, we have also plotted in figure 5 the Brillouin scattering measurements of Harley et al. [10]. All energies have been normalized to the room-temperature energy. Comparison of neutron- and light-scattering results is of interest because with neutrons we probe the lattice dynamics with applied frequencies greater than the expected range of hopping frequencies of fluorines (\( \sim 1 \text{ cm}^{-1} \)). Brillouin scattering on the other hand is concerned with excitations of \( \sim 0.5 \text{ cm}^{-1} \), comparable with or less than hopping frequencies. Figure 5 shows that for all acoustic modes at high temperatures, and particularly for the longitudinal modes, the neutron measurements imply stronger renormalization of the phonons than do the light scattering measurements. An explanation of these effects requires further neutron studies at lower energy transfer. Figure 5 also shows that both neutron- and light-scattering detect more rapid softening of the longitudinal modes than of the transverse modes in the vicinity of \( T_c \). Since longitudinal modes modulate the bulk strain field this observation is consistent with a view that transition to an anion-disordered state takes place because of interactions between the defects and their associated strain fields [15], though because of the lack of effect on \( a_0 \) we must conclude that this is a short range effect.

We have studied quasielastic neutron scattering effects in \( \text{PbF}_2 \) at high temperatures using the INS time-of-flight spectrometer at ILL Grenoble with resolution 0.2 meV. We observe no quasielastic intensity for momentum transfers \( Q \) in the range 0.1-2.0 Å\(^{-1} \). This implies either that the quasielastic width is very narrow or that scattering intensity in the quasielastic energy region is dominated by effects other than from the diffusing ions, such as coherent scattering from anharmonic phonon modes. The former interpretation
lends support to the molecular dynamics calculations of disorder in CaF$_2$ by Rahman (2) who finds quasi-elastic widths an order of magnitude less than $Q^2 D$ as expected for liquid-like motion with diffusion constant $D$. It is hoped that quasi-elastic neutron scattering measurements to be carried out shortly on SrCl$_2$ may be more conclusive. The diffusing chlorine ions here have significant incoherent cross-section so that any quasielastic effects should be better defined than in the purely coherent scatterer PbF$_2$.

3. Conclusions. — The defect dynamics of fast-ion conductors are extremely complex and at the present time are very poorly understood. Fluorite crystals, because of their structural simplicity, appear to be the most tractable of the systems investigated so far. However, even for these crystals a range of experimental techniques is required, covering both thermodynamic and spectroscopic properties.

Our neutron scattering measurements suggest the following conclusions. A simple model of interstitialcy disorder is not compatible with neutron powder-diffraction data for the high temperature disordered phases of PbF$_2$ and SrCl$_2$. Lattice expansion measurements imply that the halogen interstitial-vacancy pair does not produce an appreciable effect on the lattice parameter in PbF$_2$ and SrCl$_2$ whereas impurity-induced interstitials do cause such an effect in CaF$_2$ [17]. Inelastic neutron scattering has shown anharmonic effects consistent with disorder of the anion lattices in PbF$_2$, SrCl$_2$ and BaF$_2$ at temperatures above $T_c$. The optic modes transform into a broad smooth frequency-response while the acoustic modes remain reasonably well defined but show increasingly large anharmonic effects as the temperature approaches the melting points. Interesting differences are observed between the acoustic mode frequencies measured by neutron scattering and light scattering. Further experimental work is required to establish the frequency dependence of this softening of acoustic modes in the vicinity of $T_c$. Further quasi-elastic scattering measurements, to be carried out shortly, should throw light on the low-frequency diffusive motion of the anions. High-temperature densities of phonon states, which can only be obtained through neutron scattering, are also highly desirable. Such data will be of considerable help in understanding Raman-scattering spectra. Perhaps the most crucial requirement of all is for precise measurements of the temperature dependence of Bragg peaks to provide reliable information on the nature and extent of the disorder.

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References

DISCUSSION

R. J. FRIAUF. — You have implied that the amplitude factors indicate an amplitude of vibration amounting to several nearest neighbor distances. This sounds like a very unphysical model. It might be better to contemplate instead some distributions of Fluorine interstitial ions. In any case, there does not seem to be a very satisfactory explanation.

M. H. DICKENS. — The anomalous increase in the anion temperature-factors in PbF₂ and SrCl₂ which we observe at high temperature certainly implies extensive disorder in the anion lattice. In analysing the nature and extent of this disorder we have not yet been able to differentiate between thermal motion effects in an ordered lattice as compared with some structural redistribution representing thermally induced defects. It would of course be unphysical to attribute the large temperature factors merely to very large amplitude harmonic vibrations of the anions.

Hj. MATZKE. — It would be interesting to learn something about the possible consequences of the dynamic disorder in the anion sublattice above about 0.8 \( T_m \) on the disorder in the metal sublattice. If one is dealing with isolated randomly situated anion defects, then via the Frenkel defect equilibrium between anion defects and the Schottky equilibrium between anion vacancies and cation vacancies, there should be a corresponding change in disorder in the metal sublattice. Ca diffusion in CaF₂ does not seem to indicate any anomaly—this might be an indication of some order between the defects in the fluorine sublattice (possibly antiphase boundaries). Also, this question has a technological relevance. The nuclear fuel UO₂ which is isomorphic with the earth alkaline fluorites, might show a similar phase transition at, say, about 2 200 °C. In advanced reactors, much of the fuel may be above this temperature. None of the fuel performance codes, to my knowledge, allows for this disorder. Any information on this point would therefore be very important.