PHONONS IN SUPERIONIC CONDUCTORS
W. Hayes

To cite this version:
W. Hayes. PHONONS IN SUPERIONIC CONDUCTORS. Journal de Physique Colloques, 1981, 42 (C6), pp.C6-167-C6-174. <10.1051/jphyscol:1981650>. <jpa-00221586>

HAL Id: jpa-00221586
https://hal.archives-ouvertes.fr/jpa-00221586
Submitted on 1 Jan 1981

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
PHONONS IN SUPERIONIC CONDUCTORS

W. Hayes

Clarendon Laboratory, University of Oxford, United Kingdom

Abstract - Detailed information about the nature of disorder in superionic conductors can be obtained from the study of vibrational excitations using Raman, Brillouin and neutron scattering techniques. The present review will be concerned with the application of these techniques to materials such as AgI, CaF$_2$ and sodium β-alumina, with emphasis on the latter.

1. Introduction. - Most ionic solids have values of the electrical conductivity $\sigma$ immediately below the melting temperature $T_M$ about four orders of magnitude smaller than in the melt. In LiF, for example, $\sigma$ increases from $10^{-10} (\Omega \text{cm})^{-1}$ at room temperature to $10^{-3} (\Omega \text{cm})^{-1}$ just below $T_M = 1140$ K. On melting $\sigma$ increases discontinuously to $10 (\Omega \text{cm})^{-1}$. However, some ionic solids have values of $\sigma$ in the crystalline state comparable to that in molten solids and are referred to as superionics or fast-ion conductors. This high value of $\sigma$ is due to ionic transport and is a consequence of extensive disorder in a component sublattice of the solid. The study of ionic vibrations in disordered systems has an intrinsic interest of its own and in superionics such studies throw light on the mechanisms of conduction.

The superionic materials that have been subject to the most extensive study at a fundamental level in recent years may be divided into 3 groups:

(i) Silver and copper based compounds e.g. AgI, RbAg$_4$I$_5$ and Cul, in which disorder occurs in the silver and copper sublattices. Here the prototype material is AgI. At room temperature AgI has the hexagonal wurtzite structure and is referred to as β AgI. At $T_C = 147$C a first-order phase change occurs to a body-centred cubic structure, referred to as α AgI. The value of $\sigma$ just below $T_C$ is $\sim 3 \times 10^{-4} (\Omega \text{cm})^{-1}$; it increases abruptly at $T_C$ to $\sim 1.3 (\Omega \text{cm})^{-1}$ and falls slightly from this value on melting. A variety of structural studies indicates that in the α phase the iodine ions form a fairly rigid bcc lattice and that the silver ions are randomly distributed between them in tetrahedral interstitial sites. It also appears that the motion of Ag$^+$ ions between nearest-neighbour tetrahedral sites is the basic step in ion conduction. Phonon studies on AgI and other materials in this group have been reviewed recently and will not be discussed further here. However, the attempts that have been made to obtain information about the dynamics of the mobile ions using quasielastic light scattering and quasielastic neutron scattering should be mentioned.

(ii) Materials with the fluorite structure. These will be discussed in §2.
(iii) Materials with the $\alpha$ alumina structure. These will be discussed in §3.

2. Crystals with the Fluorite structure. - A pronounced heat anomaly occurs in halides with the fluorite structure at a temperature $T_c$ well below $T_M$; for CaF$_2$, $T_c = 1430$ K and $T_M = 1633$ K. This anomaly is due to development of extensive disorder in the anion sublattice and is associated with the onset of high ionic conductivity. A study of the effects of anharmonicity ($T < T_c$) and lattice disorder ($T > T_c$) on the Raman spectrum of CaF$_2$, SrF$_2$, BaF$_2$, SrCl$_2$ and PbF$_2$ was made by Elliott et al.

In these materials the $T_{2g}$ Raman-allowed phonon broadens with increasing $T$ and the detailed shape of the Raman band below $T_c$ can be explained quite well using third and fourth-order anharmonicity. Additional scattering develops on the low energy side of the $T_{2g}$ phonon for $T > T_c$ and this can be accounted for by a theory of defect-induced scattering, including effects of both anion vacancies and anion interstitials.

Effects of disorder in the superionic phase of fluorites ($T > T_c$) on elastic constants was studied by Brillouin scattering techniques, showing a dramatic fall of $C_{11}$ at $T_c$. Neither $C_{12}$ nor $C_{44}$ is appreciably affected by the disorder. Similar results have been obtained by neutron scattering techniques. The different behaviour of the elastic constants may be rationalised from the fact that the contributions to $C_{11}$ from Coulomb and short-range forces have the same sign whereas for $C_{12}$ and $C_{44}$ they have opposite signs. It seems that effects of defects on $C_{12}$ and $C_{44}$ is small because the change in Coulomb and short-range forces largely cancel each other.

It should be emphasised that the theories used to account for effects of disorder on the Raman and Brillouin spectra of fluorites are not sensitive to the precise configurations of vacancies and interstitials. However, very useful information has been obtained about the structure of the superionic state of fluorite.

Fig. 1: Model of a 2:2:2 defect in fluorite showing two anion interstitials, two relaxed anions and two anion vacancies.
fluorites from the \( q \)-dependence of the intensity of quasielastic neutron scattering. These results may be explained quite well assuming the existence of a transient vacancy-interstitial complex of the so-called 2:2:2 type (Figure 1), involving two anion vacancies, two anion interstitials and two relaxed anions. The neutron linewidths suggest that these complexes survive in the superionic state for times of \( \sim 1 \) ps. This type of complex is very stable and its formation contributes to the large reduction in anion Frenkel energy needed to account for the onset of cooperative disorder at \( T_{\text{f}} \).

Brillouin scattering techniques have also been used to study effects on \( T_{\text{f}} \) of doping with trivalent cations. It was found, for example, that doping \( \text{CaF}_2 \) with 9 mole per cent of \( \text{YF}_3 \) reduces \( T_{\text{f}} \) from 1430 K to \( \sim 1200 \) K. In the doped material 2:2:2 type complexes form, similar to that shown in Figure 1, but involving \( \text{Y}^{3+} \) in cation sites, rather than anion vacancies. Calculation showed that such complexes act as traps for thermally generated anion interstitials, thus reducing the energy of formation of anion Frenkel pairs and also of \( T_{\text{f}} \).

3. Compounds with the \( \beta \)-alumina structure. - Melt-grown crystals of sodium \( \beta \)-alumina have the formula \((1+x)\text{Na}_2\text{O}:2\alpha\text{Al}_2\text{O}_3\), where \( x \sim 0.3 \) represents departure from stoichiometry. The ionic conductivity at room temperature is large (\( \sim 0.04 \Omega^{-1}\text{cm}^{-1} \)) due to nonstoichiometry. The crystals have a centrosymmetric structure with hexagonal symmetry. They consist of spinel-like \((\text{Al}_{11}^{11} \text{O}_{16}^{-})\) blocks separated by mirror planes containing sodium and oxygen ions (Figure 2). The spinel blocks are \( 11.26 \) \( \AA \) thick along the \( c \) axis. The oxygen ion in the mirror plane (O(5) in Figure 2) is coordinated by \( \text{Al}^{3+} \) ions in the spinel blocks, joining the blocks together. In effect, each mirror plane is a hexagonal network of O(5) ions interspersed with cation sites referred to as Beevers-Ross (BR) and anti-Beevers-Ross (aBR), which have site symmetry \( D_6 \), and mid-oxygen (mo) which has site symmetry.
Neutron diffraction studies by Roth et al.\textsuperscript{14} on sodium $\beta$-alumina at room temperature indicate that $\sim 66\%$ of the Na$^+$ ions are near BR sites, $\sim 30\%$ are near mo sites and $\sim 4\%$ are near aBR sites. These studies also led to the suggestion that charge compensation for the excess sodium in the mirror plane occurs through interstitial oxygens, O$_1^{2-}$, in mo sites bound by two aluminium ions (Al(1) in Figure 2) displaced from their normal positions towards the O$_1^{2-}$.

Studies of the Raman spectrum of sodium $\beta$ alumina showed $E_{2g}$ peaks at 61 and 100 cm$^{-1}$.\textsuperscript{15,16} The 61 cm$^{-1}$ peak was assigned to vibrations of Na$^+$ ions in BR sites and the 100 cm$^{-1}$ peak to shearing of spinel blocks. The infrared absorption spectrum measured with the electric vector in the mirror plane is much more complex.\textsuperscript{17} However, interpretation is assisted by measuring the absorption of material approximating to stoichiometry (Figure 3a). Here excitations are sharp (FWHM $\sim 5$ cm$^{-1}$) compared to the widths of the overlapping bands found for the nonstoichiometric material (FWHM $\sim 25$ cm$^{-1}$) (Figure 3b). Since we expect the occupation of BR sites to be predominant in the more stoichiometric material we assign the 59 cm$^{-1}$ line in Figure 3a to $E_{1u}$ vibrations of Na$^+$ ions near BR sites, consistent with the assignment of the Raman peak.\textsuperscript{15,16} The other lines in Figure 3a are due to complexes of Na$^+$ ions in various degrees of association with O$_1^{2-}$\textsuperscript{17} and there is a one-to-one correspondence with the bands of Figure 3b.

Figures 3b and 3c show the change in the infrared absorption of nonstoichiometric material on going from 2 to 300 K. The intensity of the 102 cm$^{-1}$ band is very sensitive to temperature, decreasing with increasing temperature with an
activation energy of \( -0.02 \text{ eV} \). This may be taken to be the energy required to remove an extra Na\(^+\) ion from the vicinity of O\(_i^2\), making it available for long-range conduction. The 85 cm\(^{-1}\) band decays with increasing temperature with a similar activation energy. The intensity of the 135 cm\(^{-1}\) band is less temperature sensitive and the intensity of the 176 cm\(^{-1}\) band shows little change between 2 and 300 K. If, in comparison with Figure 3a, we assume that the Na\(^+\) ions giving rise to the main peak in Figure 3c are near BR sites we conclude, in agreement with Roth et al\(^{14}\), that 66% of the Na\(^+\) ions occupy such sites at room temperature. However, it would seem that the assignment by Roth et al\(^{14}\) to no sites cannot, in our case, refer to a unique complex since at least five different centres are involved. The percentage assigned by Roth et al\(^{14}\) to aBR sites is too small to be readily recognisable in our studies, but it seems likely that ions in aBR sites will have a vibrational frequency comparable to that of BR sites. Our results are in general agreement with the suggestion of Wolf\(^{18}\) that the sodium ions should be considered as two major groups, those bound with different strengths to O\(_i^2\)-i.e. in associated areas and those not appreciably perturbed by O\(_i^2\)-i.e. in unassociated areas.

We have carried out similar studies on silver\(^{19}\) and potassium B-alumina\(^{20}\) and more recently on sodium B\(^{\prime}\) alumina and its isomorphs\(^{21}\). We shall give a preliminary account of our work on sodium B\(^{\prime}\) alumina here. This material is similar in structure to sodium B-alumina. It has the rhombohedral space group D\(_{3d}^5\) and is composed of spinel-like blocks of aluminium oxide, but ordered in a triple stacking sequence along the c axis. These blocks are separated by conduction slabs containing sodium and oxygen ions. The ideal structure is represented by the formula unit Na\(_2\)O\(_2\)MgO\(_0.5\)Al\(_2\)O\(_3\) with Mg\(^{2+}\) ions dissolved primarily in tetrahedrally-coordinated Al\(^{3+}\) sites. Figure 4 shows a projection of the positions of Na\(^+\) ions in the conducting slab on to the plane defined by the bridging O\(_i^2\)-ions. The sites which

Fig. 4: Conduction slab of sodium B\(^{\prime}\) alumina showing oxygen ions (large circles), sodium ions (small circles) and a sodium vacancy (square).
correspond to the BR and aBR positions in sodium $\beta$ alumina (Figure 2) are in this case equivalent. It is generally assumed that the crystals are not stoichiometric, containing about 15% of $Na^+$ vacancies, and that the high ionic conductivity ($\sim 0.06 \Omega^{-1}\cm$ at room temperature) is due to vacancy motion.

Figure 5a shows the infrared absorption at 2K of a crystal of sodium $\beta''$ alumina provided by W.L. Roth, with the electric vector of the radiat ion perpendicular to the $c$ axis. The spectrum is complex, showing some similarity to that of sodium $\beta$ alumina (Figure 3). An approximate deconvolution of overlapping bands is shown in Figure 5. The interpretation of these bands is at present tentative awaiting the outcome of model calculations and further experiments. The bands at 155 and 176 cm$^{-1}$ are probably due to $Na^+$ ions in association with $O_2^-$. The band at 90 cm$^{-1}$ loses about half of its intensity on warming to room temperature (Figure 5b) and by analogy to sodium $\beta$ alumina may be due to $Na^+$ ions weakly bound to $O_2^-$. The peak at 65 cm$^{-1}$ increases in intensity on warming to room temperature and is probably due to $Na^+$ ions on normal lattice sites without any other defects nearby. The bands at 30 and 45 cm$^{-1}$ decrease on warming to room temperature and may be due to sodium-vacancy complexes. These are also indications of a weak band at $\sim 78$ cm$^{-1}$.

The discussion given above suggests that at room temperature about 45% of the sodium ions are on lattice sites without other defects nearby and that the rest of the sodium ions form a variety of complexes. This behaviour is similar to that of sodium $\beta$ alumina, but, again, the situation is more complex than the diffraction results for sodium $\beta''$ alumina suggest.

4. Conclusions. - The superionic materials already discussed divide into two categories from the point of view of Raman and infrared studies of phonons:

(1) A sublattice of the material is effectively totally disordered as in a AgI or partly disordered as in fluorites. The disorder here is intrinsic and is a cooperative, thermally-induced phenomenon. The characteristic features of these materials
are a Raman spectrum corresponding to a defect-induced single-phonon density of states and a quasielastic peak associated with diffusive motion.

(II) Nonstoichiometric materials, such as sodium $\beta$ alumina, where the disorder is present in as-grown crystals. The ions responsible for conductivity in these materials give rise to relatively sharp Raman and Infrared lines, giving detailed information about environment. There is a need for quasielastic light-scattering studies of these materials.

References
