Low Frequency Lattice Absorption in $RbAg_4I_5$ Solid Electrolyte

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Far infrared transmission and reflexion measurements were performed on polycrystalline samples of α-$RbAg_4I_5$ solid electrolyte. As in α-AgI, an anomalous broad low frequency absorption band centred at $5 \cdot 10^{11}$ Hz is found in addition to the lattice absorption at ca. $3 \cdot 10^{12}$ Hz. Since it is rather temperature insensitive, the low frequency band indicates the existence of very slow high amplitude lattice vibrations in this material.

Structurally disordered ionic crystals like α-AgI and others have been known since early in this century[1]. In these phases, which are usually stable at elevated temperatures, the number of possible cation sites by far exceeds the number of cations. Being always surrounded by vacant neighbouring sites the cations can move rather freely within the anion lattice. Ionic conductivities in these phases are typically of the order of $1\,(\Omega\,\text{cm})^{-1}$.

In 1966 several compounds of the composition MAg_4I_5 were discovered[2, 3] which exhibit structural disorder and high cation mobilities at room temperature. M represents Rb, K, or NH_4. Of these compounds α-$RbAg_4I_5$ has been studied most extensively as it is the most stable in the presence of moisture. At 25 °C its ionic conductivity is ca. $0.2\,(\Omega\,\text{cm})^{-1}$ (3). The structure of α-$RbAg_4I_5$ was determined by Geller[4, 5]. A unit cell contains four formula units. The arrangement of the I^- ions is similar to that of the Mn atoms in β-manganese. The I^- ions provide 56 tetrahedral sites for the 16 Ag^+ ions per unit cell, while the Rb^+ ions are located in distorted I^- octahedra. The tetrahedral sites are arranged in such a manner as to allow easy passage for the Ag^+ ions.

Although the ionic conduction of α-$RbAg_4I_5$ and other structurally disordered phases has been rather thoroughly investigated along with their structure, little attention has yet been paid to the vibrational movements of the ions in these compounds. Hoshino[6], in order to explain his X-ray data of several cation-disordered high temperature phases, had to introduce very large Debye factors for the metallic ions, and in the case of α-AgI for the anions as well. The mean ionic displacements thus obtained e. g. for α-AgI were comparable to the distances of nearest neighbouring cation sites. More recently, an anomalous broad low frequency absorption band was found in α-AgI[7]. This absorption extends at least to frequencies as low as $2 \cdot 10^{11}$ Hz, and disappears as soon as the sample is cooled below the transition point at 147 °C. Low frequency high amplitude lattice vibrations might provide an explanation. Far infrared measurements have now been carried out on α-$RbAg_4I_5$ to find out whether very low frequency infrared absorption is a common feature of cation disordered solid electrolytes.

The infrared measurements on α-$RbAg_4I_5$ were performed with the Fourier spectrophotometers LR 100 and FS 720 from Beckman Instruments Ltd., in which a lamellar grating and a Michelson interferometer are used, respectively. Transmittances of thin samples (~ 0.02 cm) and reflectivities of thick samples (~ 0.3 cm) were determined at 10^{-2} Torr in the frequency range from $2 \cdot 10^{11}$ Hz to 10^{13} Hz. The samples were plates of polycrystalline bulk material formed from the melt. An X-ray analysis of ground samples yielded the well-known lines of α-$RbAg_4I_5$[2]. The complex permittivity $\varepsilon^* = \varepsilon' - \mathrm{i}\,\varepsilon''$ and the conductivity $\sigma = \varepsilon_0\,\varepsilon''\,\omega$ were calculated from the measured quantities (ε_0 = permittivity of the vacuum, ω = angular frequency), cf. [7].

Figure 1 shows the far infrared dispersion of the conductivity of α-$RbAg_4I_5$ at 20 °C. In contrast to the maxima of $\varepsilon''(\omega)$, those of $\sigma(\omega)$ indicate the

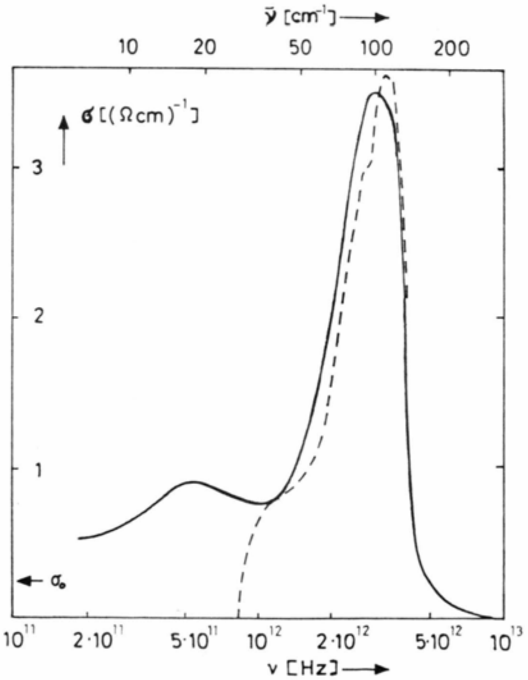

Fig. 1. Far infrared dispersion of ionic conductivity in $RbAg_4I_5$ (———) and AgI (– – –) at 20 °C. The dc conductivity of $RbAg_4I_5$ is denoted by σ_0.

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transverse mode frequencies of a crystal for any degree of damping [8]. The mutual consistency of permittivity and conductivity was checked by a Kramers-Kronig analysis.

Above 10^{12} Hz α-$RbAg_4I_5$ exhibits a normal lattice absorption spectrum which does not differ much from that of AgI at the same temperature [7]. Below this frequency there is a broad absorption band similar to that in α-AgI. While the dc conductivity of α-$RbAg_4I_5$ at 20 °C is lower than that of α-AgI at 250 °C by about one order of magnitude, the very far infrared conductivity maxima differ only by a factor of two.

For an interpretation it is important that Bloch's theorem is not valid in a crystal with structural disorder. Therefore sets of absorption frequencies should be observed. There is some similarity to the broad absorption bands of polar liquids in the submillimetre region which are interpreted as "smeared out liquid lattice bands" [9, 10]. In ionic crystals, far infrared absorption bands beyond the Reststrahlen region are usually due to multiphonon difference processes [11]. However, as the intensity of difference bands is rather temperature sensitive, their contribution can be roughly estimated from the temperature dependence of the absorption. At present, besides room temperature measurements, far infrared spectra of α-$RbAg_4I_5$ have been observed at -40 °C and at $+125$ °C. In these spectra, the shape and the strength of the band are hardly altered. In the temperature range from -40 °C to $+125$ °C, where the dc conductivity changes by a factor of seven, the conductivity maximum at ca. $5 \cdot 10^{11}$ Hz rises by not more than 15 per cent. The low frequency absorption in α-$RbAg_4I_5$ therefore should not be entirely due to multiphonon processes.

Thus we can say that the silver ions in α-AgI and α-$RbAg_4I_5$ participate in very low frequency, high amplitude vibrations in shallow effective potentials which are largely determined by the locations and movements of the other cations.

A more detailed exposition of our results is being prepared.

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