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To cite this version:
| P. Brüesch, T. Hibma, W. Bührer. PHONONS AND IONIC CONDUCTIVITY IN THE TWO-DIMENSIONAL SUPERIONIC CONDUCTOR AgCrS₂. Journal de Physique Colloques, 1981, 42 (C6), pp.C6-178-C6-180. <10.1051/jphyscol:1981652>. <jpa-00221588>

HAL Id: jpa-00221588
https://hal.archives-ouvertes.fr/jpa-00221588
Submitted on 1 Jan 1981

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PHONONS AND IONIC CONDUCTIVITY IN THE TWO-DIMENSIONAL SUPERIONIC CONDUCTOR AgCrS₂

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Abstract.- Far-infrared technique, coherent and incoherent neutron scattering have been used to study the lattice dynamics of AgCrS₂ at different temperatures. The low frequency TO mode shows a pronounced softening between 10 K and 700 K. The data are analyzed with a rigid-ion model and it is shown that the pattern of eigenvectors of the low energy modes ($\nu < 45 \text{cm}^{-1}$) give basic information for the diffusion process of the Ag ions.

AgCrS₂ is a layer crystal which shows rather anisotropic behaviour in structure and macroscopic properties. At 673 K AgCrS₂ exhibits a second order phase transition to a partially disordered structure where the Ag ions are distributed over a large number of available sites, resulting in a high ionic conductivity in the layers (1). Insight into the fast diffusion can be gained by investigating not only static properties such as $\sigma (0)$ but rather the full dynamics of the crystal lattice. This paper reports results of far-infrared and neutron inelastic scattering experiments. The measurements are analysed with a rigid-ion model and the process of jump-diffusion is discussed on the basis of a reaction coordinate which is expressed in terms of the phonon structure.

AgCrS₂ crystallizes in a trigonal lattice (space group $C\overline{3v}$) with one formula unit per primitive cell. At the zone center, the irreducible representations are $\Gamma = 4\ A_1 + 4\ E$, and both types are infrared active. Along the trigonal axis and at the point T there are again 4 one-dimensional and 4 two-dimensional representations; all other points in the Brillouin zone have lower symmetry. Single phase AgCrS₂ has been prepared as described elsewhere (1). Small additions of AgCl improved the growth of single crystal platelets.

The far-infrared (FIR) measurements have been performed with a Beckmann interferometer in the polarizing mode for $\nu < 150 \text{cm}^{-1}$ and in the Michelson mode for $150 \text{cm}^{-1} < \nu < 400 \text{cm}^{-1}$. Fig. 1 shows the transmission spectrum of an AgCrS₂ film on Si, and Fig. 2 displays the reflectance spectrum of a pressed pellet. The first absorption band near $30 \text{cm}^{-1}$ can be interpreted as TO mode ($\vec{q} || \vec{z}$, $\vec{e}(\vec{q}) \perp \vec{z}$) an assignment which is based on transmission measurements of a thin single crystal.
A rich structure is observed between 190 cm\textsuperscript{-1} and 400 cm\textsuperscript{-1}, a tentative assignment is given on Fig. 1.

The dispersion relation of the lowest energy modes was determined by coherent inelastic neutron scattering techniques on a small but perfect single crystal. For the experiments the triple axis spectrometer at the reactor Saphir was used in its doubly focusing mode of operation (2). Results for phonons propagating along the trigonal axis (r - T) and along (r - L) are shown in Fig. 3. The dispersion curves show the typical behaviour of an anisotropic layer compound with its large separation in intralayer and interlayer modes.

FIR measurements as function of temperature showed a pronounced softening of the lowest TO mode, the frequency decreases from 39 cm\textsuperscript{-1} at 10 K to 22 cm\textsuperscript{-1} at the transition point, Fig. 4. This mode softening is unique in the large family of Ag based superionic conductors (3). The symmetry of the AgCrS\textsubscript{2} lattice is low, and hence group theory gives only little information on the eigenvectors of the ions in the different modes. Therefore it is necessary to perform a model calculation, and as a starting point we used a simple rigid ion model with valence field forces for the short range term. The parameters (10 short-range stretching constants and ionic charges) were adjusted in order to reproduce the lowest frequency modes (Fig. 3).

A serious problem is given by the large separation between the lowest in-plane mode (30 cm\textsuperscript{-1}) and the corresponding out-of-plane mode (190 cm\textsuperscript{-1}) which could not satisfactorily be explained with our model. For a deeper understanding of this anisotropy the influence of the induced permanent dipoles on the sulphur ions must be included in the computations (4). However we obtain a good agreement for the low frequency modes and due to the large energetic separation of modes with the
same symmetry, the eigenvectors of the lowest branches turned out to be almost model independent. We obtain the following result: \( \Gamma \) (TO) (30 cm\(^{-1}\)) Ag planes vibrate against the rigid S-Cr-S layer; \( \Gamma \) (TA) only Ag ions involved; \( \Gamma \) (TO) (45 cm\(^{-1}\)) only S-Cr-S layer in motion; \( L \) (TA) (45 cm\(^{-1}\)) only Ag vibrates. Atomic migration in crystals is discussed by Flynn (5). The instantaneous relative position of the migrating atom and its neighbours is of central interest in the diffusion process and is a suitable reaction coordinate which can be expressed in terms of the phonon structure (eigenvectors, density of states). Evidently low lying flat optic modes and low zone boundary acoustic branches give the main effects because they have a large density of states, strong vibrational amplitudes and are thermally easily activated; moreover in all these modes in AgCrS\(_2\) the Ag ions and the surrounding cage move not in phase. In addition the softening of the frequencies will enhance the diffusion probability (reduced barrier height). This can, in prinicipale, give rise to a temperature dependent activation energy (1).

In summary we conclude that the observed dynamical features, i.e flat, soft, low energy modes, qualitatively explain the fast diffusion of Ag ions in AgCrS\(_2\). For a theory of the conductivity \( \sigma (\nu, T) \) and the transition temperature \( T_c \), additional experiments at higher temperatures as well as a better lattice dynamical model are necessary.

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