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Quasielastic neutron scattering from a single crystal of α-AgI

K. Funke (*), A. Höch and R. E. Lechner (**)

Institut für Physikalische Chemie and Sonderforschungsbereich 126, Göttingen, West Germany

Résumé. — On donne les premiers résultats des expériences de diffusion quasiélastique de neutrons par un monocristal d'α-AgI. Des spectres de durée de vol ont été obtenus pour plusieurs orientations du cristal. Le changement du vecteur d'onde était de l'ordre de $1{,}0\ \text{Å}^{-1} \lesssim |\mathbf{Q}_0| \lesssim 1{,}8\ \text{Å}^{-1}$ pour la diffusion élastique.
Comme pour les matériaux polycristallins les spectres consistent typiquement en une composante large et en une composante étroite de diffusion quasiélastique. La composante étroite montre une anisotropie marquée due à l'anisotropie translationnelle à travers les sites tétraédriques. La composante large des spectres est pratiquement isotropique et peut être attribuée à un mouvement localisé et irrégulié.

Abstract. — A first report is given on a quasielastic neutron scattering experiment performed on a large single crystal of α-AgI. Time-of-flight spectra were taken at 250 °C, under different orientations of the crystal. The range of wavevector transfer was $1.0\ \text{Å}^{-1} \lesssim |\mathbf{Q}_0| \lesssim 1.8\ \text{Å}^{-1}$ for elastic scattering.
As in the case of polycrystalline material the spectra typically consist of a broad plus a narrow quasielastic component. The narrow line shows pronounced anisotropy, reflecting the anisotropy of translational diffusion paths via tetrahedral voids. The broad wings of the spectra are essentially isotropic and correspond to an irregular local motion.

1. **Introduction.** — In this paper we give a first report on a quasielastic neutron scattering experiment performed on a large single crystal of α-AgI. The high-temperature phase of silver iodide has become famous as the prototype of the so-called fast ion conductors. Quasielastic neutron scattering is one of the most powerful techniques available for studying the dynamics of diffusion on an atomic scale. In the present neutron-scattering experiment we have for the first time used a single crystal of α-AgI, in order to analyse the microscopic directionality of the elementary diffusion steps.

Valuable information has already been supplied by earlier experiments. In one of these a single crystal has been used for determining the structure of α-AgI by neutron diffraction [1]. It could be shown that the probability density map of the silver ions has maxima at the tetrahedral voids of the bcc iodide lattice. It was hence suggested that the translational diffusion of the silver ions essentially consists of hops from one tetrahedral void to another. In the following we shall sometimes use a short-hand notation : *tetrahop* motion.

In other *precursor* experiments the diffusion dynamics in α-AgI was studied by quasielastic neutron scattering from polycrystalline samples [2-4]. The spectra generally consisted of a relatively narrow quasielastic line superimposed on a much broader distribution. The quasielastic broadening of the narrow line is due to translational diffusion, while the broad wings reflect a more rapid local motion of the silver ions. Since an experiment on polycrystalline material is not sensitive to any microscopic directionality of diffusion, *tetrahops* could not be resolved.

One of the aims of the present experiment has been the observation of the anisotropy of the narrow quasielastic component in order to test the tetrahop model and others for conformity. Secondly it also appeared interesting to check whether directional resolution would decompose the broad quasielastic part of the spectrum into inelastic phonon peaks.

2. **Experimental.** — For the preparation of the crystal, the Bridgman technique was used. The crystal was grown in a closed quartz container and was of conical shape. Having a volume of roughly 16 cm^3 it was clear and transparent to the eye. After preparation the crystal was kept hot in order to avoid destruction by the $\alpha \rightarrow \beta$ phase transition at 147 °C. In particular, it was transported from Göttingen to Grenoble by car at a temperature of roughly 250 °C.

Spectra were taken at the multichopper time-of-flight spectrometer IN5 of the Institut Laue-Langevin at Grenoble. During the experiment, the crystal was kept at 250 °C. It could be rotated about its axis (angle ψ) for changing its orientation. The wavelength of the incoming neutrons was chosen to be 6.2 Å ; Bragg reflections could thus be excluded. The crystal was analysed in reflection geometry with

(*) *Present address* : Institut für Physikalische Chemie und Elektrochemie, Callinstraße 3-3A, Hannover, West Germany.
(**) Hahn-Meitner-Institut, West Berlin, Germany.

scattering angles φ ranging from 60° to 130°. This corresponds to a range of wavevector transfer $|\mathbf{Q}_0|$ (for elastic scattering) from 1.0 $Å^{-1}$ to 1.8 $Å^{-1}$. The energy resolution (FWHM) was 70 μeV. The experimental data were corrected for background and container scattering and for self-shielding. Transformation to an energy scale yielded spectra $S^{tot}(\psi, \varphi, \omega)$ containing both incoherent and coherent scattering.

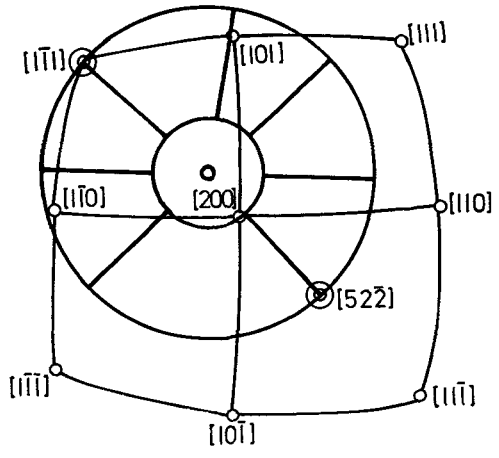

Fig. 1. — Orientation of the crystal axis and the experimental vectors of momentum transfer (at $\hbar\omega = 0$) with respect to some principal crystallographic directions.

Figure 1 shows the orientation of the sample axis and of experimental vectors of momentum transfer, $\hbar\mathbf{Q}_0$, with respect to some principal crystallographic directions. The crystal axis is the centre of the stereographic projection, and the vectors $\hbar\mathbf{Q}_0$ are represented by points lying along seven straight lines. These correspond to seven experimental values of the rotation angle ψ and $60° \lesssim \varphi \lesssim 130°$.

In the following we will restrict ourselves to a brief discussion of the particular spectra obtained with $\hbar\mathbf{Q}_0$ along the two directions marked in figure 1, namely [1$\bar{1}$1] and [52$\bar{2}$], with $|\mathbf{Q}_0| = 1.82$ $Å^{-1}$.

3. **Results and discussion.** — The two spectra given in figure 2 are typical in two respects. First, they show a marked anisotropy of the narrow component. Second, the wings at $\hbar\omega > 1$ meV are almost identical.

Let us discuss the second point first. Comparison of various spectra taken at identical scattering angles φ, but at different angles ψ, indeed proves that the shape of the broad component is essentially isotropic and does not display any pronounced structure. In spite of being similar in shape, the individual spectra at constant φ but different ψ differ in their absolute counting rates. This simply signifies an anisotropy of the diffuse structure factor $S(\mathbf{Q})$, since most of the scattering is coherent. The differences in the absolute values of $S^{tot.}$ diminish with increasing momentum transfer suggesting that the anisotropy

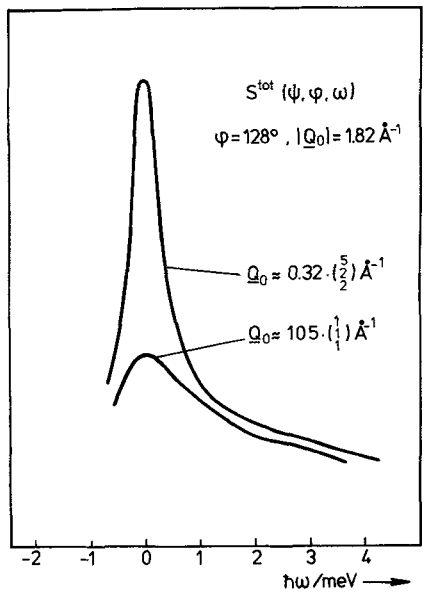

Fig. 2. — Corrected spectra for two vectors of momentum transfer $\hbar\mathbf{Q}_0$ (at $\hbar\omega = 0$); $S^{tot.}$ in arbitrary units.

of $S(\mathbf{Q})$ becomes weaker with increasing $|\mathbf{Q}|$. Since simultaneously the orientational average of $S(\mathbf{Q})$ (i.e. $S(Q)$ for the powder [3]) approaches unity, this means that the quasielastic spectrum becomes essentially determined by the single-particle motion. The broad quasielastic component is hence not to be attributed to well-defined low-energy phonons, but rather to an irregular single-particle local motion [4]. Recently it has been suggested that this kind of motion is performed by each silver ion within a dynamic cage created by the repulsive Coulomb interaction with its moving neighbours [5, 11].

In contrast to the broad wings of the spectra, the shape of the narrow line is found to be markedly anisotropic, in particular at relatively large values of momentum transfer. In figure 2, the extreme example is that with $\mathbf{Q}_0$ parallel to a $\langle$ 111 $\rangle$ direction. In this case the central component is extraordinarily flat. The other spectrum, with $\mathbf{Q}_0$ parallel to a $\langle$ 522 $\rangle$ direction, is relatively similar to others taken at the same scattering angle.

Let us now try to check the predictions from the tetrahop model by comparison to the experimental spectra. Generally speaking, the situation is less advantageous than for hydrogen in metals since silver is mainly a coherent scatterer. To a certain extent one can overcome this difficulty by measurement of the diffuse structure factor in all $\mathbf{Q}$-space and by relating the coherent scattering law to $S_{inc.}(\mathbf{Q}, \omega)$ and $S(\mathbf{Q})$, cf. [6]. The relation

$$S(\mathbf{Q}, \omega) = S_{inc.}(\mathbf{Q}.S^{-1/2}(\mathbf{Q}), \omega).S(\mathbf{Q})$$

is of course neither exact nor does it take any particular correlation effects into account. However, it satisfies the second moment. Higher moments can be satisfied

in more elaborate relations. At present, our own measurements of $S(\mathbf{Q})$ are not yet completed and the treatment indicated above must be postponed. It will be given in our full paper.

A *direct* comparison of the experimental spectra $S^{\text{tot.}}_{\text{exp.}}(\psi, \varphi, \omega)$ and calculated spectra $S_{\text{tetrahop,inc.}}(\mathbf{Q}, \omega)$ is however possible and reasonable at relatively large $\mathbf{Q}$ and small ω. In this case the shape of $S^{\text{tot.}}_{\text{exp.}}(\mathbf{Q}, \omega)$ is already largely determined by $S_{\text{inc.}}(\mathbf{Q}, \omega)$, and the asymmetry of $S^{\text{tot.}}_{\text{exp.}}(\psi, \varphi, \omega)$, due to ψ, φ = constant instead of $\mathbf{Q}$ = constant, does not yet impede a direct comparison. The above requirements are roughly fulfilled for the narrow quasielastic component observed at our largest scattering angle.

For the calculation of $S_{\text{tetrahop,inc.}}$ a modified Chudley-Elliott model can be used [7]. For fixed $\mathbf{Q}$, $S_{\text{tetrahop,inc.}}(\mathbf{Q}, \omega)$ is then a sum of six Lorentzians. The widths and weights of these can be computed from the eigenvalues and eigenvectors of a hermitian 6 × 6 matrix.

For the spectra of figure 2, $S^{\text{tot.}}_{\text{exp.}}$ and $S_{\text{tetrahop,inc.}}$ are compared in figure 3.

It is immediately seen that the experimental and calculated spectra are in good agreement with each other.

Mathematically, the relatively broad spectrum calculated for $\mathbf{Q}$ parallel to a ⟨ 111 ⟩ direction results from the shape of the particular 6 × 6 matrix. From its six eigenvectors, all weight factors except the third are found to be zero. The width of the calculated spectrum is therefore only determined by the third eigenvalue, while in other directions the first two (smaller) eigenvalues are responsible for relatively narrow lines.

From figure 3 the tetrahop model appears to be a reasonable first approximation for describing the translational diffusion of the silver ions in α-AgI. Nevertheless it must be noted that the view of random hops among tetrahedral voids has to be modified on both the short and long time scales.

On the short time scale the tetrahop model cannot explain the broad wings of the experimental spectra. This holds true although the spectra have not been taken at constant $\mathbf{Q}$. Instead, we assume a more or less irregular diffusive local motion within the cage formed by the neighbouring ions [5]. In terms of a

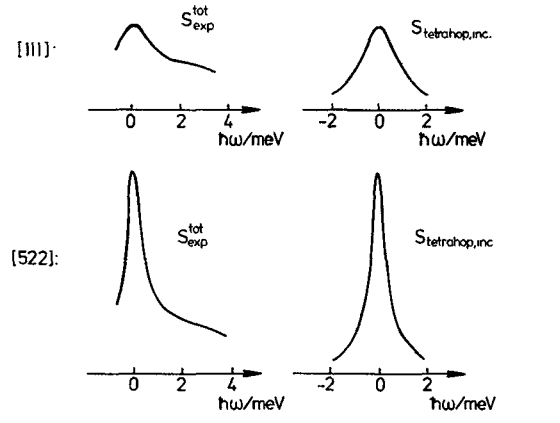

Fig. 3. — Comparison of experimental spectra and the incoherent scattering law calculated from the tetrahop model.

modified tetrahop model this would mean the frequent occurrence of *bounce-back* forward-backward hops [5, 8]. Interestingly this feature was also found by Vashishta and Rahman in their molecular-dynamics study [9].

On the long time scale, i.e. at $\sim 10^{-11}$ s, pronounced correlations of the single- and many-particle motion of the silver ions do exist. This is known from the conductivity spectrum in the microwave range [10] and from the Haven ratio. Relatively long times have been introduced earlier [4, 5] by visualizing silver ions which — once in a while, i.e. after a few tetrahops — get locally trapped by their neighbours. The mean *time of translational tetrahop diffusion*, τ_1, would be largely determined by the density of the mobile ions [11].

A further analysis of our present spectra might help to clarify the actual deviations from the simple tetrahop model.

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