PHYSICAL REVIEW B VOLUME 23, NUMBER 9 1 MAY 1981

Temperature dependence of the Raman depolarization ratio in α-AgI

G. Mariotto, A. Fontana, and E. Cazzanelli
Dipartimento di Fisica dell'Università di Trento, 38050 Povo (Trento), Italy
and Gruppo Nazionale di Struttura della Materia, Università di Trento

F. Rocca
Istituto per la Ricerca Scientifica e Tecnologica, Trento, Italy

M. P. Fontana
Istituto di Fisica, Università di Parma, Parma, Italy

V. Mazzacurati and G. Signorelli
Istituto di Fisica, Università di Roma, Roma, Italy

(Received 4 December 1980)

In this note we present the relevant results of a detailed study of the temperature dependence of the depolarization ratio of Raman scattering in superionic AgI. We confirm previous data of Raman intensity showing an order-disorder transition at 430 °C.

In recent work[1] on the temperature dependence of Raman spectral intensity in α-AgI, we have presented corroborating evidence for an order-disorder-type transition, occurring at about 430 °C. The existence of such a transition has already been conjectured on the basis of thermodynamic data and calculations.[2,3] Although it is common in the literature[4–6] to assume that the AgI sublattice "melts" at the superionic transition temperature, and that thereafter the Ag ions move quasifreely within the cage of the cubic iodine sublattice, the Ag ions in the α phase still retain some degree of local ordering. This residual correlation of Ag ions is due to the nonrandom occupation of the 42 crystallographic sites available to Ag in the O_h^9 space-group structure of the iodine cage.[7] The order-disorder transition at 430 °C [also observed in $RbAg_4I_5$ at 208 K (Ref. 8)] would correspond to the complete randomization of the Ag ions over all the available sites. In our previous work[1] we have shown that the depolarized one-phonon density of states, which dominates the Raman spectrum in α-AgI, rapidly decreases in intensity as the temperature of 430 °C is approached. We had interpreted this result as evidence for the loss of polarizability anisotropy on the local level, due to the randomization of Ag positions about the iodine ions taking place in the neighborhood of 400–430 °C.

In this note we present further evidence which confirms our interpretation and therefore the existence of an order-disorder transition in the "melted" Ag sublattice.

We have measured the spectral dependence of the degree of depolarization of Raman spectra as a function of temperature in the superionic phase of AgI. The experimental details of our measurements have already been described in Ref. 1. The polarized Raman spectra were taken in a backscattering geometry: $Z(YY)\bar{Z}$ for $I_{\parallel}(\omega)$ and $Z(YX)\bar{Z}$ for $I_{\perp}(\omega)$, where Z is the c axis in the β phase of AgI (wurtzite structure). The depolarization characteristics of our measuring apparatus were determined by viewing the light elastically diffused by a piece of paper placed at the sample site, upon excitation with an ordinary filament lamp. Using a quartz polarization scrambler before the entrance of the double monochromator, we found that the degree of polarization of the scattered light was less than 1%: thus at the precision level of our measurement, our apparatus did not introduce any spurious polarization. We have checked furthermore to determine whether the temperature variation of the Raman depolarization ratio might be influenced by macroscopic changes taking place in the sample. For this we followed the behavior of the depolarization ratio of the elastically scattered and reflected light at zero-frequency shift. In our previous work we had already verified that the intensity of such light did not vary in temperature; we have found that the same holds true for the relative depolarization ratio. Thus the macroscopic optical characteristics of our sample were found to be temperature independent in the range of interest here. Furthermore no sample degradation occurred, as shown by the reproducibility of our data over repeated cycles.

In Fig. 1 we show the Raman spectra taken at 170 °C (i.e., about 23 °C above the superionic transition temperature) and 430 °C. The spectra were taken over the frequency range 7–165 cm^{-1}. From these spectra it is clear that $I_{\perp}(\omega)$ is nearly equal to $I_{\parallel}(\omega)$ for all frequency shifts, as 170 °C, thus yielding a frequency-independent depolarization ratio

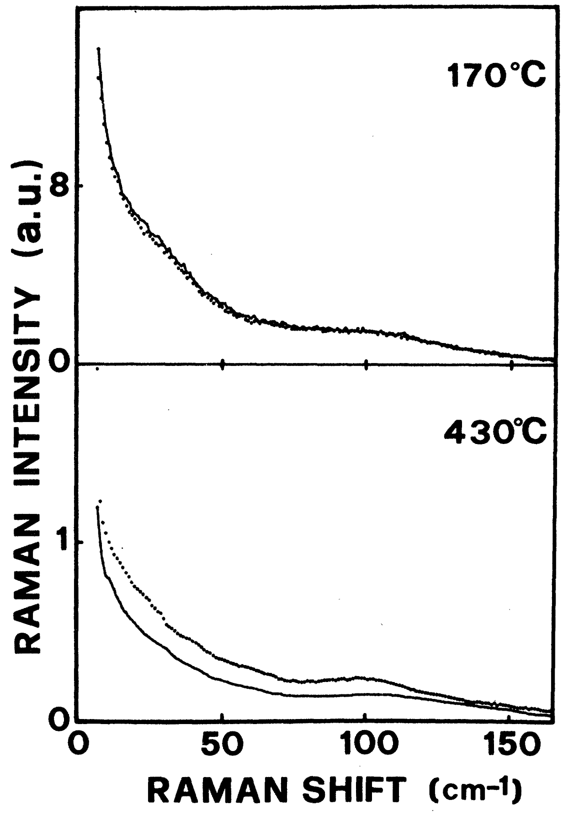

FIG. 1. Experimental Raman spectra from 7 to 165 cm^{-1} in two polarizations. Dots are in $Z(YY)\bar{Z}$ geometry; solid lines are in $Z(YX)\bar{Z}$ geometry. Note the inversion of intensity at the two different temperatures.

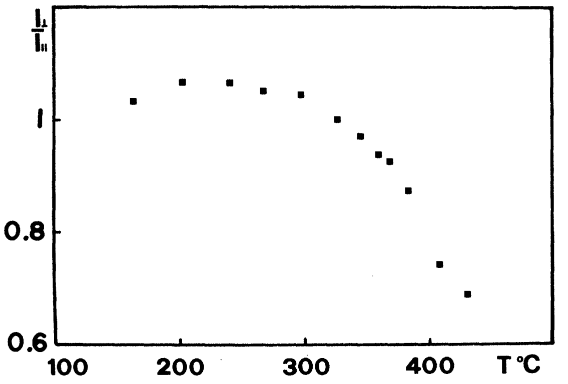

FIG. 2. Plot of the depolarization ratio $I_\perp/I_\parallel$ at increasing temperature from 170 to 430 °C.

$\rho = I_\perp/I_{\parallel}$) approximately equal to unity. At 430 °C $I_\perp$ is smaller than $I_\parallel$ by about 30%, yielding $\rho \simeq 0.7$; furthermore a noticeable deviation of $\rho(\omega)$ from this value at low frequencies may be observed. This difference in the frequency behavior of $\rho(\omega)$ between 170 and 430 °C may have deeper dynamical causes; however, if we consider that it takes place at low frequencies ($\omega_s \lesssim 15$ cm^{-1}) and that it becomes noticeable at 430 °C, where the Raman intensity has decreased by about one order of magnitude from the value observed at 170 °C, then the most likely cause of the discrepancy is the instrumental tail of the elastically scattered light, which instead remains constant in intensity in this temperature range. Thus we consider the slight frequency dependence of $\rho(\omega)$ at 430 °C to be spurious and use for ρ the average value for $\omega \geqslant 20$ cm^{-1}.

In Fig. 2 we report the behavior of ρ versus temperature. It may be noticed that $\rho \simeq 1$ until about 330 °C; above this temperature ρ begins to decrease towards the value of about 0.7 at 430 °C.

We have already shown[1] that there is no softening in the Raman spectral distribution as a function of temperature; thus, as for the case of the intensity, the changes in the depolarization ratio reported here must be connected with changes in the local ordering of the Ag ions. The iodine sublattice has fcc cubic structure; therefore we expect that its contribution to the total Raman polarizability may be neglected compared with the contribution due to the motion of the Ag$^+$ ions relative to the iodine ions. Thus when the local correlation—and hence polarizability anisotropy—in the Ag "melted" sublattice decreases and finally disappears at about 430 °C, the depolarization ratio must tend to the value characteristic of totally depolarized scattering from an isotropic fluid, i.e., $\rho = \frac{3}{4}$. This expected behavior is clearly verified by the experimental data reported in this note.

This work is partially supported by Consiglio Nazionale delle Ricerche, under Contract No. CT 80.00816.11.

---

[1] A. Fontana, G. Mariotto, and M. P. Fontana, Phys. Rev. B 21, 1102 (1980).

[2] C. M. Perrott and N. H. Fletcher, J. Chem. Phys. 50, 2770 (1968).

[3] C. M. Perrott and N. H. Fletcher, J. Chem. Phys. 52, 3368 (1970).

[4] Fast ion transport in solids, see *Solid State Batteries and Devices*, edited by W. van Gool (North-Holland, Amsterdam, 1975).

[5] *Superionic Conductors*, edited by W. D. Maham and W. L. Roth (Plenum, New York, 1976).

[6] H. Wiedersich and S. Geller, in *Chemistry of Extended Defects in Solid Electrolytes*, edited by L. Eyring and M. O'Keeffe (North-Holland, Amsterdam, 1970), p. 629.

[7] L. W. Strock, Z. Phys. Chem. Abt. B 25, 441 (1934).

[8] R. Vergas, N. D. Salomon, and C. P. Flynn, Phys. Rev. Lett. 37, 1550 (1976).