

Raman spectroscopic evidence of a continuous order-disorder transition in superionic α -AgI

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A careful determination of the temperature dependence of the integrated Raman scattering intensity and spectral shape of superionic AgI is reported from 150 to 500 °C. The Raman intensity is found to vary according to the law expected for first-order scattering up to 320 °C; for higher temperatures the intensity decreases by more than one order of magnitude over a temperature range of about 60 °C. Currently a temperature dependence of the Raman normalized spectral shape was also observed. The data are interpreted on the basis of the possibility of an order-disorder-like transition, which takes place in the same temperature region in which specific-heat anomalies have been reported.

The structure and dynamics of superionic AgI has been an interesting challenge for theoreticians and experimentalists for many years.¹

The well-known anomalously high ionic conductivity of this prototype superionic conductor in its α phase ($T_0 = 147$ °C) has been associated with a so-called partial melting transition, in which the Ag^+ sublattice "melts" while the I^- sublattice remains rigid and ordered.

The positive ion "fluid" is then assumed to be distributed in some random fashion among the many available crystallographic sites of the O_h^2 space group structure of the α phase, with the ions jumping "quasifreely" from one site to the other. The theoretical study on such system is of course quite complex, in particular, because it seems that for α -AgI permanence times on a given site and jump times from site to site are of the same order of magnitude ($\tau \sim \tau_0 \sim 10^{-13}$ sec at $T = 150$ °C), therefore making the customary asymptotic-model approximation (free jump diffusion on one hand and heavily damped oscillatory motion on the other) inappropriate.

Another difficult problem is the proper estimation of the role of correlation effects between the cations themselves and between the diffusing cation and the "rigid" anion lattice, which cannot be assumed to provide simply a static periodic potential.

That such correlation effects should exist and have considerable influence on the dynamics of this "partially melted" system is shown by simple steric considerations involving the ionic radii (R) of the constituent ions [$R(\text{Ag}^+) = 1.26$ Å, $R(\text{I}^-) = 2.16$ Å; lattice parameter = 2.84 Å] and by the fact that at the superionic transition the iodine sublattice distorts.

Crucial experimental evidence for the existence of

short-range correlations within the "melted" AG sublattice is given by the behavior of the specific heat of AgI as a function of temperature.² Provided the sample is nominally "pure" (i.e., of near perfect stoichiometry), the specific heat increases monotonically through the α phase to a temperature of 430 °C, above which it drops rapidly to a constant value of $C_p \approx 15$ cal/mole °C. This behavior is quite suggestive of an order-disorder phase transition and has been so interpreted.³ Since the thermodynamical behavior of α -AgI is subject to some irreproducibility connected with sample stoichiometry and thermal history (some authors⁴ even question the validity of the specific-heat data themselves), it is not clear whether a true phase transition occurs at 430 °C in α -AgI. More independent measurements are needed. However the whole thermodynamical phenomenology is indicative of a temperature variation in the ordering of the Ag sublattice in the α phase. It is also natural to assume that the local ordering will decrease with increasing temperature. From the point of view of site occupation, this would mean that, in the low-temperature region of the α phase, there will be a nonuniform distribution (favoring the so-called $12d$ sites⁵) and that the distribution will become more and more uniform over all sites as temperature increases.

In this article we wish to report dynamical evidence, obtained by Raman spectroscopy, that this is indeed the case; i.e., the Ag^+ sublattice retains some form of ordering and rigidity upon transition to the α phase, and that such residual Ag^+ sublattice vanishes in a temperature region of some 60 °C about the 430 °C transition temperature reported on the basis of calorimetric data.

Our evidence consists of a careful and, we hope,

quantitative determination of the temperature dependence of the integrated Raman intensity and spectral shape of α -AgI in its entire temperature range. Such spectral density is totally depolarized and is clearly connected with the disorder in the Ag^+ sublattice and the vibrational motions of the Ag^+ ions relative to the I^- -ion "cage". Our samples were thin pale yellow clear platelets of $3 \times 3 \times 0.3 \text{ mm}^3$ dimension, kindly provided by Professor Mooser from the Lousanne Polytechnique. Control measurements were also performed on samples of different origin (provided by R. Comes of University Paris-Sud, Orsay). Only the highest quality samples from both sources gave similar and reproducible behavior.

The samples were placed in a specially built optical oven which is described elsewhere.⁶ Temperature uniformity over a volume of 0.5 cm^3 about the sample site was better than 1°C and temperature stability better than $\pm 0.2^\circ\text{C}$. Temperature was measured with a thermocouple placed directly in contact with the sample.

The sample itself was sandwiched between two micro sheets and pressed against the hot finger of the oven, which had been previously evacuated and subsequently back filled with 1 atm of dry and ultrapure He gas. We found this last step essential for our measurements, since in vacuum the sample quickly sublimated out I_2 and in an oxygen-containing environment irreversible photochemical damage of the sample took place. Details on these matters will be given in a forthcoming full report.

The sample was illuminated with $6328\text{-}\text{\AA}$ light from a 20-mW (nominal) power, at the sample site never exceeding 5 mW.

Since the optical absorption edge of AgI shifts towards the red with increasing temperature, we have carefully determined the behavior of the optical transmission of our sample as a function of temperature.

The most important result here is that, in the region of the $6328\text{-}\text{\AA}$ excitation, light the optical transmission in the α phase changes only very slightly over the whole temperature range studied.

In Fig. 1 we report the temperature dependence of the integrated Raman intensity from 10 to 190 cm^{-1} , normalized by the Bose-Einstein factor $n(\omega, T) + 1$ where $n(\omega, T) = [\exp(\hbar\omega/kT) - 1]^{-1}$. The behavior is reported for runs made on two different samples, in order to show that some sample dependence of the origin persists on the quantitative level, although the basic behavior seems to be sample independent. The Raman intensity is thus found to vary according to the law expected for first-order scattering, up to 320°C ; for higher temperature the intensity decreases rapidly over a temperature range of about 60°C . We have observed also a temperature dependence of the Raman normalized spectral shape. In Fig. 2 we show the normalized spectra taken at two significant tem-

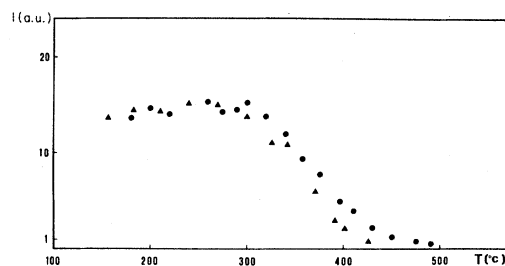


FIG. 1. Temperature dependence of integrated Raman intensity of α -AgI. The intensity is normalized by the Bose-Einstein population factor $n(\omega) + 1$. The triangles and the dots indicate runs made on two different samples.

peratures. We see clearly, especially in the normalized spectra, that the spectral features at 30 and 100 cm^{-1} behave differently with increasing temperature. This is shown more clearly in Fig. 3, where we plot the ratio of the two intensities versus temperature. Note again that the variation of the ratio indicates a critical-temperature region (400°C) in which the system seems to undergo some kind of structural or dynamical change.

Our Raman data thus confirm from this point of view the specific-heat data of Perrott and Fletcher.^{2,3} In our case, however, the so-called order-disorder transition seems to take place over an extended temperature range, instead of happening abruptly at 430°C . Whether this discrepancy is due to intrinsic differences in the experimental techniques, or is instead due to specific sample characteristics, we cannot say at this time. However the Raman behavior can be interpreted well on the basis of what is known on the structural and transport properties of α -AgI.

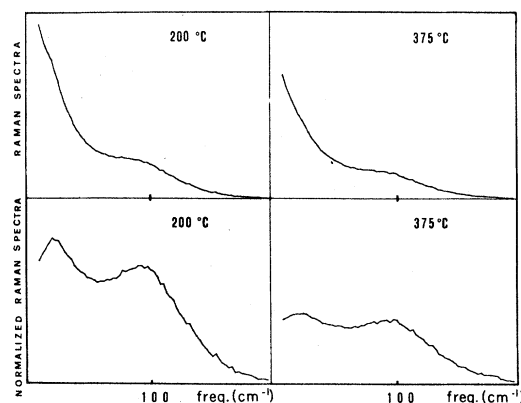


FIG. 2. Raman spectra taken at 200 and 375°C . The same spectra normalized by Bose-Einstein factor. Note how spectral features at 30 and 100 cm^{-1} , respectively, behave differently with increasing temperature.

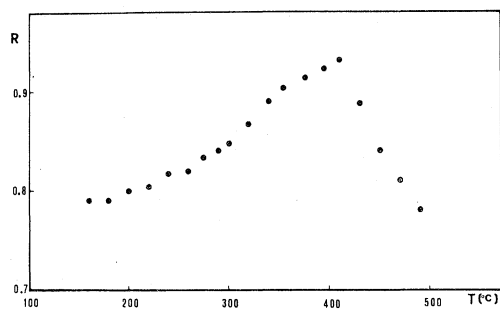


FIG. 3. Plotting of the ratio of intensity of the 100 and 30 cm^{-1} spectral features: $R = I(100 \text{ cm}^{-1})/I(30 \text{ cm}^{-1})$, vs temperature. Note again that the variation of R indicates a characteristic temperature in the region of about 400 °C.

Such a "crystal" would not show any first-order Raman scattering, since the only oscillatory motions would be connected with the I^- sublattice, which is monoatomic and has bcc structure, for which every lattice point is a center of inversion. Such a lattice would also be expected to have very weak second-order scattering. Thus, if this is indeed the situation for temperatures, say, above 500 °C, absence of detectable Raman scattering at high temperatures would be well accounted for. The temperature decrease of the integrated Raman intensity in the region of 430 °C is clearly connected with the complete disordering of the Ag^+ distribution among the three types of crystallographic sites available in the 0_h^2 structure.

In fact, the extra-mode features in the β phase and the overall spectrum in the α phase are totally depolarized. Thus, considering that in the α phase the ordinary zone-center phonon contribution is negligible, the spectral density is due only to the anisotropic part of the Raman tensor.

The polarizability anisotropy is obviously connected with the spacial distribution of the Ag^+ ions about the I^- lattice.

When the "order-disorder" transition occurs, and the Ag^+ ions are more and more evenly distributed among the available sites, the polarizability anisotropy decreases and finally becomes negligible. Correspondingly, the depolarized Raman spectral density vanishes (within the limits of our measurement). The local structure changes should be associated with changes in the dynamical responses of the system. Indeed we do observe (Fig. 3) spectral changes in the characteristic-temperature region about 430 °C. However, we should also expect a general "softening" of the spectrum due to the possible decrease in coupling between the Ag^+ ions and the I^- sublattice. Such softening does not seem to take place, at least in the temperature region where the Raman intensity remains detectable.

In conclusion, besides confirming the possibility of an order-disorder transition in α -AgI, our results show strikingly the type of dynamical anomalies which may take place in a "partially melted" system.

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