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Theoretical model for the temperature dependence of Raman scattering in α-AgI

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A new model for the distribution of the cations in α-AgI is proposed. This model explains the change in the anisotropic polarizability, as deduced by the temperature dependence of previous Raman data for temperatures below 700 K. We represent the Ag^+ ion distribution on the "cages" of d sites around each I^- ion as a local fluctuation of charge density. At increasing temperature this arrangement vanishes progressively and the Ag^+ distribution becomes homogeneous and isotropic. A simplified model of polarizability is developed to relate the theoretical dependences of Raman intensities and depolarization ratios to the experimental ones. Qualitative and quantitative agreement is obtained; hence we are confident that the Raman data indicate the existence of a cooperative correlation between silver-occupied positions which disappears at high temperature.

INTRODUCTION

In recent years there has been a renewed interest in solid electrolytes, thanks to the very high ionic conductivity shown in the temperature region far below the melting point. This phenomenon is generally accompained by a disordered spatial distribution of mobile ions. This kind of disorder coexists with the permanence of an ordered crystal structure and it seems generally independent from the thermal history of the sample.[1-4] Hence these kinds of superionic conductors are more useful than other materials (i.e., glasses) for theoretical and experimental studies on solid-state disorder.

Among solid electrolytes, AgI has been by far the most studied for many years because of its very simple chemical composition and structure. Quite a few models have been developed for the disordered Ag^+ sublattice in α-AgI. The "liquidlike" model explains the high conductivity, the high specific heat at the $\beta \rightarrow \alpha$ transition, and it has also been invoked to explain the shape of light scattering spectra.[5-8] In this model the motion of silver cations is assumed to be a continuous process, modulated by a periodic potential provided by the iodine rigid lattice. The "lattice gas" model, however starts with the assumption of a free occupancy of sublattice sites by silver atoms and a hopping motion between nearest-neighboring sites is proposed[9,10]; this model requires short jumping times with respect to the residence ones and it is based on a short-ranged Ag^+-Ag^+ correlation. More recently Andreoni and Phillips have developed a "lattice liquid" model; they take into account the Ag^+-Ag^+ Coulomb interaction to calculate the radial distribution function.[11] This introduces a correlation between the occupied positions for the silver atoms, excluding, for example, the simultaneous occupation of nearest sites.

The current models give good agreement to many experimental data of α-AgI (at low temperature), but generally do not suppose any change of order in the cation sublattice at higher temperature in the α phase, while there are some experimental evidences both of a singularity in the specific heat at 700 K,[12,13] and of a change in the activation energy of the ionic conductivity.[14] These phenomena are present also in other superionic conductors and can be compared with the M-Ag_4I_5 family (M=NH_4,K,Rb) phase transition at ~210 K,[9] and with a similar behavior observed in Ag_2S.[13] Recently, anomalous effects have also been observed in the α-AgI integrated Raman intensity[15,16] and depolarization ratio[17] below the "critical" temperature of 700 K.

Our effort to understand such data has led us to develop a simplified model for the distribution of the silver cations in the α phase as a function of temperature.[18,19] On the basis of this model we support the lattice liquid picture and introduce a temperature-dependent anisotropic distribution of Ag^+ around I^- ions.

REVIEW OF EXPERIMENTAL DATA AND OUTLINE OF THE MODEL

The Raman data as a function of temperature in α-AgI show two peculiar features we want briefly to recall the following:

(i) The reduced spectral density

$$J_{\gamma\gamma'}(\omega)=I_{\gamma\gamma'}(\omega)/[n(\omega)+1]$$

does not appreciably change its shape (see Fig. 1)[15,16] while its integral

$$J_{\gamma\gamma'}=\int_0^\infty J_{\gamma\gamma'}(\omega)d\omega$$

is quite constant as a function of temperature from the $\beta\rightarrow\alpha$ transition up to 600 K and then drastically decreases by more than one order of magnitude [see Fig. 2(a)].

(ii) The depolarization ratio,

$$R=I_{\gamma\gamma'}(\omega)/I_{\gamma\gamma}(\omega)$$

(see Fig. 3), has a frequency-independent constant value of ~ 1 in the temperature region where the integrated intensity is constant, and then decreases down the value of ~ 0.7 [see Fig. 2(b)].[17]

These experimental results have to be examined keeping in mind some structural properties which have been already reported for α-AgI. Indeed, while the I^- sublattice is a bcc structure with two iodine per unit cell, the Ag^+ "quasifree" ions constitute a disordered sublattice, due to the high number of available equilibrium positions which well exceed the cation number in the crystal. To clarify this point, in Fig. 4 we report the possible sites for Ag^+ ions just around a single iodine.[20]

The 24 solid circles are called *d* sites; they have a tethraedral coordination to the nearest-neighbor iodines and have to be considered equivalent. Triangles are called *h* sites (trigonal coordination), while the squares are *b* sites (digonal coordination). It is generally recognized that the occupation of *d*

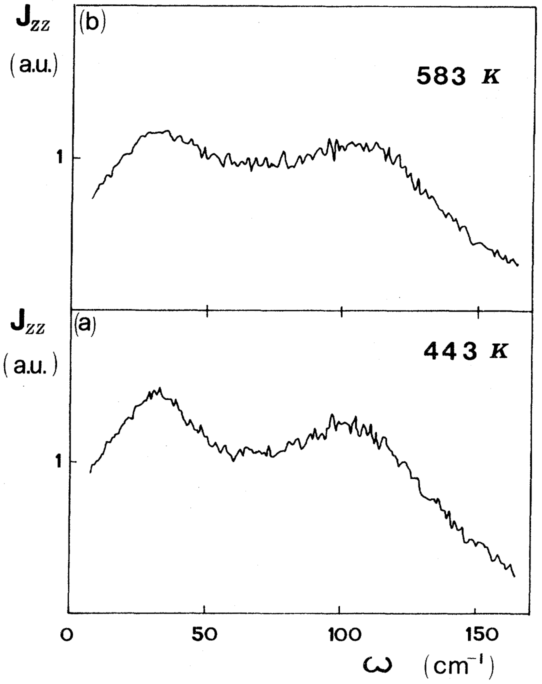

FIG. 1. Raman spectral density $J_{zz}(\omega)$ vs ω in α-AgI for 180° scattering angle. (a) $T=443$ K; (b) $T=583$ K.

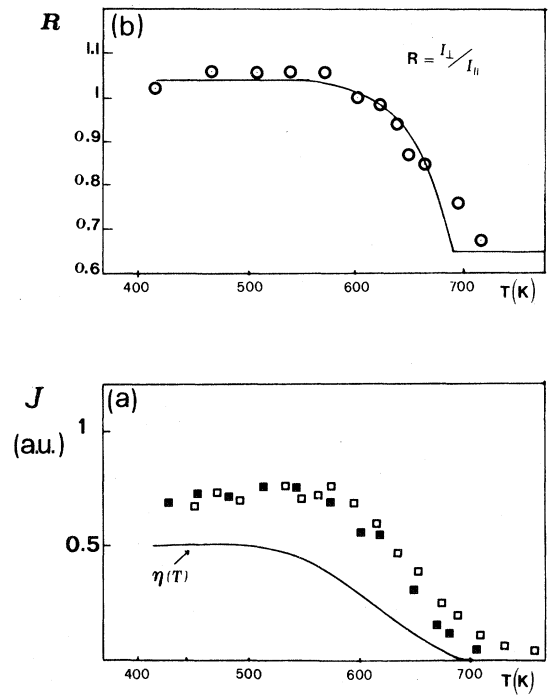

FIG. 2. (a) Squares represent the experimental values of the integrated Raman intensity $J_{zz}(T)$ as a function of temperature, obtained by two different runs. Solid curve indicates the behavior of the fractional number $\eta(T)$ obtained from $J_{zz}(T)$ as explained in the text. (b) Open circles are the experimental values of the depolarization ratio $R(T)=J_{xz}(T)/J_{zz}(T)$ versus temperature. Solid curve is the theoretical value of $R(T)$ obtained using $\eta(T)$ of Fig. 2a (see text).

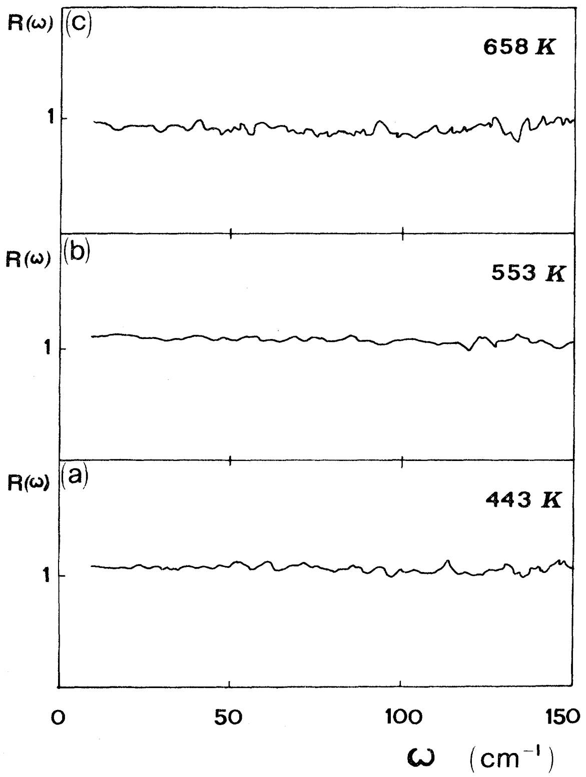

FIG. 3. $R(\omega,T)=J_{xz}(\omega,T)/J_{zz}(\omega,T)$ as a function of frequency shift. (a) $T=443$ K; (b) $T=553$ K; (c) $T=658$ K. Obviously, the $R(T)$ experimental values reported in Fig. 2(b) (open circles) are $R(T)=\sum_{i=1,N}R(\omega_i,T)/N$.

sites is preferred, while *b* sites are nearly unoccupied and *h* sites have an intermediate occupation probability.[21] It can be easily seen that, even if we neglect the occupation of the *h* and *b* sites, the *d* sites available for the Ag^+ create a sublattice, whose points exceed the number of silver atoms. In this way it is possible to arrange the Ag^+ in a very high number of different configurations, giving rise to a highly disordered distribution.

As far as the ionic conductivity is concerned, in the jump model already mentioned the Ag^+ ion passes from a *d* site to another via the intermediate *h* site (which may be considered a long-lived excited state.[22])

From these considerations we may deduce some properties of the Raman spectrum. In the limiting case of a perfectly disorderd Ag^+ fluid, the motion of the silver ions is negligibly coupled to the mechanical oscillations of the I^- lattice. Therefore, in the lattice liquid picture, the dynamics of the mobile ions and that of the iodine sublattice should be nearly uncorrelated. Since the dynamics of the two subsystems is well separated in frequency, the mobile atoms will contribute to the scattering process only within a few wave numbers from the exciting line (with a nearly "Lorentzian" line shape), while the iodines ions can contribute in the acoustical and optical phonon regions of their bcc sublattice.

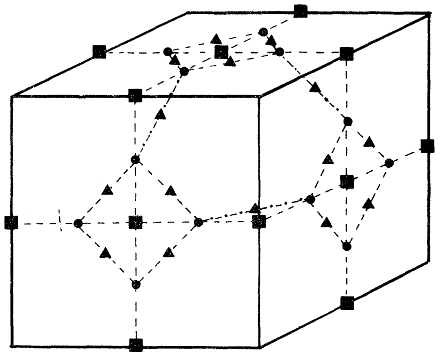

FIG. 4. Allowed sites for the Ag^+ ions in α-AgI as reported in current literature (see text). ● *d* sites; ▲ *h* sites; ■ *b* sites. The I^- ions occupy the corners and the center of the cube.

Because of symmetry selection rules the Raman spectrum of a bcc regular lattice of iodine atoms cannot give first-order Raman scattering. Therefore if we neglect the polarizability of the silver ions the Raman spectrum will arise entirely from disordered polarizability components modulated by the iodine's motion. On the other hand, the only way to have a disordered polarizability on the bcc iodine lattice is to induce on each I^- ion a polarizability which depends on the silver-iodine relative positions. Such a mechanism would yield a disordered-allowed one-phonon Raman spectrum related to the overall density of states of the iodine lattice[15,23] in reasonable agreement with the observed spectrum. As a consequence the integrated intensity and the depolarization ratio *R* must be directly related to the distribution of silver ions around an iodine ion.

The simplified polarizability model we propose takes into account all these considerations and allows a quantitative analysis of the experimental results. It is well known that the Raman scattering intensity may be written as

$$I_{\gamma\gamma'}(\omega)\propto\int dt\,e^{-i\omega t}\int d^3r_1\int d^3r_2\,e^{i\vec{q}\cdot(\vec{r}_1-\vec{r}_2)}\times\langle P_{\gamma\gamma'}(r_1,t)P_{\gamma\gamma'}(r_2,\phi)\rangle\,, \tag{1}$$

where $\gamma = x,y,z$ are the directions of the polarization vector of the exciting and scattered light, $\omega = \omega_i - \omega_s$ is the frequency shift, and $\vec{q} = \vec{k}_i - \vec{k}_s$ the exchanged wave vector. $P_{\gamma\gamma'}(\vec{r},t)$ represents the macroscopic polarizability tensor, and the angular brackets indicate the thermal average. As already pointed out,[24,25] the macroscopic quantity $P_{\gamma\gamma'}(\vec{r},t)$ may be calculated for molecular crystals as a sum of "effective" molecular polarizabilities located on each scattering site, evaluating afterward the thermal and configurational averages. In our model for the AgI crystals, we look at each iodine ion as the elementary scattering source, and assume that the polarizability anisotropy is induced by the local electric field due to the surrounding silver ions. Other mechanisms, such as modulation or orientation of partially covalent bonds, can also be invoked. The result will depend on the silver-ion arrangement which will be characterized by a temperature dependent parameter. A test of self-consistency for the model will be to calculate both intensities and depolarization ratios using this single parameter. Under certain approximations discussed below, the model yields a closed expression for the spectrum.

THE DISORDERED-ALLOWED RAMAN SPECTRUM IN AgI

Using Eq. (1) together with the assumptions made previously we may write down the expression for the induced Raman spectrum in α-AgI. The simplest way to do this is to consider the Ag^+ positions as fixed for a sufficiently long-lasting time with respect to the I^- oscillatory motions. This is done noting that the Ag^+ diffusive motion is related to the nearly Lorentzian component already quoted,[25] the linewidth of which is smaller than the vibrational frequencies considered in this paper. The leading contribution to the vibrational spectrum will arise from the polarizability term[24]

$$\sum_{\alpha}\sum_{a}\sum_{il}\left[\frac{\partial P^{il}_{\gamma\gamma'}}{\partial X^{\alpha}_{ila}}\right]\delta X^{\alpha}_{ila}(t) ,$$

where X^{α}_{ila} is the α Cartesian component of the instantaneous mutual distance between the iodine i ($i=1,2$) in the cell l ($l=0,\ldots,N$) and the silver ion a (the index a running on all the occupied d sites in the crystal), $P^{il}_{\gamma\gamma'}$ is the induced polarizability on the (i,l) iodine. If $\vec{u}_{il}(t)$ is the displacement of such an ion from its equilibrium position $\vec{x}_{il}$ and $\vec{R}_{il}(t) = \vec{u}_{il}(t) + \vec{x}_{il}$, Eq. (1) becomes[24]

$$I_{\gamma\gamma'}(\omega) \propto \int dt\, e^{-i\omega t} \sum_{il}\sum_{i'l'}\sum_{aa'}\sum_{\alpha\beta} \frac{\partial P^{il}_{\gamma\gamma'}}{\partial X^{\alpha}_{ila}} \frac{\partial P^{i'l'}_{\gamma\gamma'}}{\partial X^{\beta}_{i'l'a'}} \langle u^{\alpha}_{il}(t) u^{\beta}_{i'l'}(0) e^{i\vec{q}[\vec{R}_{il}(t) - \vec{R}_{i'l'}(0)]} \rangle . \tag{2}$$

With the assumption of complete orientational disorder of these polarizability derivatives, it has already been shown[24] that (2) reduces to

$$I_{\gamma\gamma'}(\omega) \propto \int dt\, e^{-i\omega t} \sum_{il}\sum_{aa'}\sum_{\alpha\beta} \frac{\partial P^{il}_{\gamma\gamma'}}{\partial X^{\alpha}_{ila}} \frac{\partial P^{il}_{\gamma\gamma'}}{\partial X^{\beta}_{ila'}} \langle u^{\alpha}_{il}(t) u^{\beta}_{il}(0) \rangle . \tag{3}$$

If we recall that in a bcc structure the averaged Cartesian components of the atomic displacements must be equivalent, we have in the harmonic approximation

$$I_{\gamma\gamma'}(\omega) \propto \left\langle \left[\sum_{a}\sum_{\alpha} \frac{\partial P^{il}_{\gamma\gamma'}}{\partial X^{\alpha}_{ila}} \right]^2 \right\rangle_{\text{av}} \frac{[n(\omega)+1]}{\omega} \rho(\omega) , \tag{4}$$

where the notation $\langle\ \rangle_{\text{av}}$ indicates a configurational average and $\rho(\omega)$ is the density of vibrational states.[26]

Disregarding the spectral shape, we can simply derive from Eq. (4) the integrated reduced Raman intensity

$$J_{\gamma\gamma'} = \int_0^{\infty} d\omega \frac{I_{\gamma\gamma'}(\omega)}{n(\omega)+1} \propto \left[\int_0^{\infty} d\omega \frac{\rho(\omega)}{\omega} \right] \left\langle \left[\sum_{a\alpha} \frac{\partial P^{il}_{\gamma\gamma'}}{\partial X^{\alpha}_{ila}} \right]^2 \right\rangle_{\text{av}} . \tag{5}$$

In the harmonic approximation $\int d\omega[\rho(\omega)/\omega]$ is constant, hence $J_{\gamma\gamma'}$ depends on temperature only through the configurational average in the right-hand side of Eq. (5). In the framework of our polarizability model, owing to the symmetry properties of the electric field, the induced polarization may be written as[27]

$$P^{il}_{\gamma\gamma'} = P^{il}[\mathcal{E}^2_{il}(t)] f_{\gamma\gamma'}(t) , \tag{6}$$

where

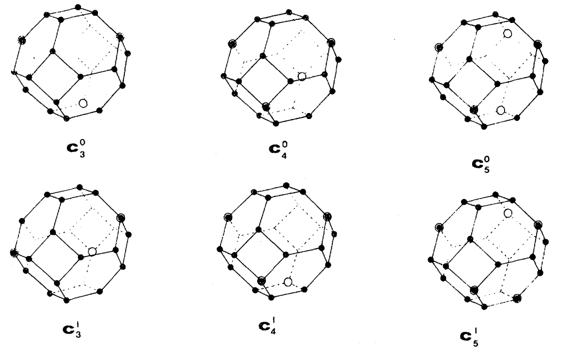

FIG. 5. Lowest energy sets of configuration in a single d-site cage C_n^k, with $n=3,4,5$ and $k=0,1$.

$$f_{\gamma\gamma'}(t)=\mathscr{E}_{il}^{\gamma}\mathscr{E}_{il}^{\gamma'}/\mathscr{E}_{il}^{2}-\tfrac{1}{3}\delta_{\gamma\gamma'}$$

are the usual Legendre polynomials and, for small values of the electric field,

$$P^{il}(\mathscr{E}_{il}^{2})=p\,\mathscr{E}_{il}^{2}(t) \tag{7}$$

p being a constant. In our approximation the electric field $\vec{\mathscr{E}}_{il}(t)$ must be evaluated in the geometrical center of the iodine atom, and it can be written as

$$\mathscr{E}_{il}^{\gamma}=q^{*}\sum_{a}\frac{X_{ila}^{\gamma}}{|\vec{X}_{ila}|^{3}} \tag{8}$$

with q^* the effective charge of the silver ion. Therefore the expression for the polarizability derivatives, appearing in Eq. (5), may be formally written as the sum of two terms

$$\frac{\partial P_{\gamma\gamma'}^{il}}{\partial X_{ila}^{\alpha}}=pf_{\gamma\gamma'}\frac{\partial \mathscr{E}_{il}^{2}}{\partial X_{ila}^{\alpha}}+p\,\mathscr{E}_{il}^{2}\frac{\partial f_{\gamma\gamma'}}{\partial X_{ila}^{\alpha}}\ . \tag{9}$$

The first term corresponds to a modulation of the field intensity on the iodine, while the second corresponds to a fluctuation in the field direction. Hence the effective charge that has to be inserted in the first term is connected with the Szigeti dynamical charge[28] $q_s^*=0.65e$, since it contains the derivatives of the field strength. In the second term the effective charge value does not appear in the derivatives because the instantaneous direction of the field does not depend on the charge of the silver atoms, while the electric field modulus is calculated in the equilibrium position of the nuclei, so that it has to be connected directly with the ionicity of the crystal,[29] i.e., $q_p^*=0.77e$. The electric field of Eq. (8) may be exactly evaluated extending the summation only to the silver ions contained in a sphere around the iodine (i,l), outside of which the charge neutrality may be imposed as a strict condition. Nevertheless we may approximate this value fairly well, as far as the induced polarizability fluctuations are concerned, considering only the nearest-neighbor silver atoms, because the contributions are rapidly decreasing with the iodine-silver distances. Taking into account only the nearest-neighbor silvers of each iodine, the task of evaluating the field and its derivatives appearing in Eq. (8) and (9) is oversimplified, and expression (9) assumes a very meaningful form:

$$\frac{\partial P_{\gamma\gamma'}^{il}}{\partial X_{ila}^{\alpha}}=\frac{2}{D^{3}}\,|\vec{\mathscr{E}}_{il}|\cdot[q_s^{*}\hat{\mathscr{E}}_{il}^{\alpha}(\hat{\mathscr{E}}_{il}^{\gamma}\mathscr{E}_{il}^{\gamma'}-\tfrac{1}{3}\delta_{\gamma\gamma'})+q_p^{*}(\tfrac{1}{2}\delta_{\alpha\gamma}\hat{\mathscr{E}}_{il}^{\gamma'}+\tfrac{1}{2}\delta_{\alpha\gamma'}\hat{\mathscr{E}}_{il}^{\gamma}-\hat{\mathscr{E}}_{il}^{\alpha}\hat{\mathscr{E}}_{il}^{\gamma}\hat{\mathscr{E}}_{il}^{\gamma'})]+\mathscr{Z}\ , \tag{9'}$$

where $\mathscr{Z}$ represents zero average terms. Indeed it becomes equivalent to that adopted by Burns, Dacol, and Alben[30] in their equation (3) if only the anisotropic polarizability terms are considered. The main difference is that in our expression their d_1 and d_2 are defined in terms of effective charges and fields, and cannot be used as free parameters as has been done in their previous works.[23,30] It may be noted that the value of the effective field strongly depends on the silver-ion positions in the nearest-neighbor d sites "cage" around a given iodine. This cage, shown by the solid circles in Fig. 5, is made by 24 d sites and the stoichiometric number of Ag^+ belonging to its four. Generally, we may assign n silver ions to a single cage, and it is easy to verify that many arrangements of such an environment are possible.

To proceed further let us denote by C_n^k the set of these arrangements that are obtainable from one another by every symmetry operation allowed for the cage. All these equivalent configurations belonging to each set C_n^k have both the same total energy E_n^k and field modulus $|\mathscr{E}_n^k|^2$.

Equation (5) may now be written as

$$J_{\gamma\gamma'}\propto\sum_{n}\sum_{k}W(C_n^k,T)n^{2}|\vec{\mathscr{E}}_n^k|^{2}\left[\frac{2}{3}\left[1+\frac{\delta_{\gamma\gamma'}}{3}\right]+4(\xi^{2}-1)\langle f_{\gamma\gamma'}^{2}\rangle_{C_n^k}\right]=\sum_{n}\sum_{k}W(C_n^k,T)J_{\gamma\gamma'}^{(n,k)}\ , \tag{10}$$

where

$$W(C_n^k,T)=d_n^k e^{-E_n^k/kT}\Big/\sum_{k,n}d_n^k e^{-E_n^k/kT} \tag{11}$$

denote the probability of finding a given configuration belonging to the set C_n^k at temperature T, k is the Boltzmann constant, $\xi=q_s^*/q_p^*$, and $\langle\ \rangle_{C_n^k}$ in-

TABLE I. We report characteristic quantities for some C_n^k sets. Definitions of these quantities can be found in the text. The repulsive energy values are expressed in eV and the electric field values are given in 3.08×10^4 cgs units.

Configuration	Energy	Electric field	$\langle f_{zz}^2\rangle$	$\langle f_{xz}^2\rangle$	d_n^k
C_3^0	7.84	1.0	$\frac{2}{9}$	0	72
C_3^1	7.92	1.0	$\frac{2}{9}$	0	144
C_4^0	16.5	0.0			144
C_4^1	16.7	1.41	$\frac{1}{18}$	$\frac{1}{12}$	572
C_5^0	29.2	1.0	$\frac{2}{9}$	0	1440
C_5^1	29.8	1.0	$\frac{2}{9}$	0	2880
C_2^0	2.23	0.0			24
C_6^0	47.2	0.0			5760

dicates an average over all the elements of C_n^k, the number of which is d_n^k. In Fig. 5 some of the configurations with $n=3,4,5$, are shown. As we have already pointed out, the stoichiometric occupation number for a single cage is four (configurations belonging to the C_4^k) so that the existence of a C_5^k implies a contemporary presence of a C_3^k and so on. It is easy to calculate $|\vec{\mathscr{E}}_n^k|$, $\langle f_{\gamma\gamma'}^2\rangle_{C_n^k}$, and d_n^k for each set C_n^k; in Table I we report such values for some C_n^k. The evaluation of the total energies E_n^k is on the contrary a more complicated task. As a matter of fact E_n^k contains the contribution of the following.

(a) The covalent bonding energy of the n silver atoms with the surrounding iodines.

(b) The electrostatic attractive contribution (obviously with the iodine ions contained in a neutrality sphere around each considered Ag^+).

(c) The electrostatic Ag^+-Ag^+ repulsion between the silver ions belonging to the same cage.

(d) The electrostatic Ag^+-Ag^+ repulsion with the silver ions belonging to the surrounding cages.

All these contributions are dependent on the arrangement in the cage considered, as well as on the distribution of all the surrounding ions. Nevertheless, it can be observed that, in the hypothesis of d-site occupancy only, the first two contributions must be only slightly dependent on the silver arrangement. As far as the other two contributions are concerned, it may be noted that the first one is the leading term in calculating the repulsive energy, and it is only dependent on the arrangement of the cage itself, while the second one is mainly related to the configurations of the nearest cages, relatively to the one considered.

In a first approximation we may evaluate the energies of the C_n^k, taking into account only contribution (c), which amounts to neglecting the intercage interactions. Some values of these energies are also reported in Table I. It is easily seen that the configurations, which generate a nonvanishing electric field on the iodine having the lowest possible energies, are C_4^1 and the combination $C_3^0+C_5^0$. The values of Table I can be inserted in Eqs. (10) and (11) to obtain the integrated intensities $J_{\gamma\gamma'}(T)$ and the depolarization ratios $R(T)$.

It is easily seen that since in our approximation $E_4^1<E_3^0+E_5^0$ ($\ll$ all other relevant configurations) and both $J_{\gamma\gamma'}(T)$ and $R(T)$ are increasing functions of temperature in contrast with the experimental evidence.

It may be noted, however, that in any case

$$J_{\gamma\gamma'}^{(4,1)}/J_{\gamma\gamma}^{(4,1)}=R_4^1=\frac{3}{2}\frac{1+\xi^2}{3+\xi^2}=0.68 \tag{12}$$

is very close to the depolarization ratio measured at high temperatures while

$$R_3^0=R_5^0=3/4\xi^2=1.05 \tag{13}$$

is almost coincident with its low-temperature value. This suggests that the true energies associated with the C_k^n configurations must be such to favor the presence of $C_3^0+C_5^0$ pairs at low temperatures and their annihilation into two C_4^0 or C_4^1 at high temperatures, (at about 700 K). Disregarding any effort to calculate contribution (d) explicitly we can use the experimental integrated intensities $J_{zz}(T)$ or $J_{xz}(T)$ to evaluate the fractional number of $C_3^0+C_5^0$ pairs $\eta(T)$.

Figure 2(a) shows the behavior of $\eta(T)$ versus temperature which can be now used together with the values of R_4^1 and $R_3^0=R_5^0$ to construct $R(T)$. The good agreement with the experimental results is shown in Fig. 2(b) and gives confidence to the basic hypothesis of our model.

The behavior of $\eta(T)$ implies that the energy of a pair $C_3^0+C_5^0$ in a bulk of such pairs has to be lower than the energy of $2C_4^0$, while in a bulk of C_4^k configurations the situation must be reversed. Contribution (d) might indeed be responsible for such a behavior. A very naive explanation may be given by looking at $C_4^{0(1)}$, C_3^0, and C_5^0 cages as "neutral," "negative," and "positive" cages, respectively. An electrostatic "attraction" between positive and negative cages may lower the energy of a $C_3^0+C_5^0$ pair if they are close enough; this effect can also depend on the number of C_3^0 and C_5^0 around it. Something like a cooperative ordering in the system is created in such a way that it can be thermally destroyed at increasing temperatures. From this point of view a $C_3^0+C_5^0$ pair may be regarded as an instantaneous picture of the "local charge fluctuations" invoked also by Zeyher[31] to explain the low-frequency dispersion of conductivity in α-AgI.

CONCLUSIONS

In order to explain our Raman data, we have assumed that the silver ions are distributed in the *d* sites, neglecting other possible equilibrium positions. Their distribution is not completely random, and the mobile ions can move from one site to another via the intermediate *h* site. Their motion is considered to be completely uncorrelated from the iodine oscillations.

It is assumed, furthermore, that the main contribution to the anisotropic polarizability of the system arises essentially from the iodine ions, and that it is induced on it by the silver-iodine Coulombic interaction. This is modulated both by the iodine motion (giving rise to disorderd-allowed Raman spectrum) and by the silver motion (central component observed by Winterlingh).

On the basis of such hypotheses we have proposed to explain the experimental data with the existence of a high correlation between silver ions at low temperatures, which creates local charge fluctuations and then local anisotropy in the iodine polarizability. This correlation vanishes with increasing temperature, giving rise both to a decrease in the integrated Raman intensity and in the depolarization ratio.

The silver distribution proposed is not in contrast with the Andreoni and Phillips lattice liquid model; moreover the existence of charge fluctuations is in fair agreement with the hypotheses of Zeyher.[31] We want to point out that our model does not necessarily imply the existence of a phase transition, but also does not exclude such a possibility. Other experimental data are needed to solve this intriguing question. In any case, if an order-disorder phase transition is found, Raman data indicate that the transition temperature has to be around 700 K. This can be interpreted as the temperature where the "percolation" in the C_3^0-C_5^0 cage system would be broken.

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