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Static Dielectric Function of Superionic Conductor α-AgI

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The wave-number–dependent static dielectric function of the superionic conductor α-AgI is determined by use of structural analysis data. The dielectric function indicates the existence of a static charge-density wave, which reflects the iodine sublattice. The dielectric functions of the β phase and the molten phase are also determined for comparison. We have found that the dielectric function in the molten phase resembles that of the strongly coupled one-component plasma near its fluid-solid transition.

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A group of solid materials which have a high ionic conductivity comparable to that of molten salts exist. These materials are called solid electrolytes, fast ion conductors, or superionic conductors and are of considerable interest because of their novel physical behavior.

The dielectric function is one of the most important concepts in condensed-matter physics. The dielectric function furnishes a direct measure of the dielectric response of the system and it tells us the extent to which the external field is screened by the polarization of the medium that it induces.[1] The static dielectric functions of metals,[1,2] semiconductors,[3,4] and insulators[5,6] have been studied intensively in the past years. For the superionic conductors, there are some works concerning the frequency dependence of the dielectric function.[7] However, as far as the present authors are aware no work has been realized on the wave-number–dependent static dielectric function.

The aim of this Letter is to show the static dielectric behavior of the superionic conductor α-AgI. By making use of structural analysis data, the correlation function of charge-density fluctuations is obtained. Knowing this quantity, the dielectric function may be obtained through the fluctuation-dissipation theorem. In order to emphasize the peculiar behavior of the dielectric function of the superionic conductors, the static dielectric function of β-AgI and molten AgI are also determined.

The static dielectric function is written in terms of the charge response function $\chi(\mathbf{q})$ as

$$1/\varepsilon(\mathbf{q}) = 1 + (4\pi e^2/q^2)\chi(\mathbf{q})\,. \tag{1}$$

By using the classical form of the fluctuation-dissipation theorem, the above dielectric function can be rewritten in terms of the charge-charge structure factor as

$$1/\varepsilon(\mathbf{q}) = 1 - (4\pi\rho_0 e^2/k_B T q^2)S_{ZZ}(\mathbf{q})\,. \tag{2}$$

By an analog treatment given by Bhatia and Thornton,[8] the number-number $S_{NN}(\mathbf{q})$, number-charge $S_{NZ}(\mathbf{q})$, and charge-charge $S_{ZZ}(\mathbf{q})$ structure factors are written in terms of the partial structure factors $S_{\alpha\beta}(\mathbf{q})$ as follows:

$$S_{NN}(\mathbf{q}) = \sum_\alpha\sum_\beta (c_\alpha c_\beta)^{1/2} S_{\alpha\beta}(\mathbf{q})\,, \tag{3a}$$

$$S_{NZ}(\mathbf{q}) = \sum_\alpha\sum_\beta Z_\alpha (c_\alpha c_\beta)^{1/2} S_{\alpha\beta}(\mathbf{q})\,, \tag{3b}$$

$$S_{ZZ}(\mathbf{q}) = \sum_\alpha\sum_\beta Z_\alpha Z_\beta (c_\alpha c_\beta)^{1/2} S_{\alpha\beta}(\mathbf{q})\,. \tag{3c}$$

In the above expressions, $\rho_0 = N/V$ is the number density, and $Z_{\alpha,\beta}$ and $c_{\alpha,\beta} = N_{\alpha,\beta}/N$ are the effective valence and concentration, respectively.

In a solid, $S(\mathbf{q})$ depends, in general, on the direction of $\mathbf{q}$. Since we are going to use the experimental structure data measured in a polycrystalline sample, hereafter we write simply $S(q)$ instead of $S(\mathbf{q})$. $S(q)$ represents a suitable average of $S(\mathbf{q})$ over all directions of $\mathbf{q}$.

α-AgI is one of the best known superionic conductors. β-AgI transforms at 147 °C into the high-temperature α phase which exhibits an unusually high ionic conductivity of several $\Omega^{-1}\mathrm{cm}^{-1}$. The structure of α-AgI has been extensively studied by using neutron and x-ray diffraction.[9,10] The diffraction pattern shows a clear distinction between the Debye lines and the diffuse liquidlike pattern.[10] By analyzing the x-ray scattering intensity of α-AgI, Tsuchiya, Tamaki, and Waseda[10] concluded that the liquidlike diffuse pattern consists of both Ag-Ag and Ag-I interference functions.

The number-number, number-charge, and charge-charge structure factors of α-AgI obtained from the structural data of Tsuchiya, Tamaki, and Waseda[10] are shown in Fig. 1. The spike components come from the Bragg reflection and the smooth component comes from the diffuse scattering. To obtain Fig. 1, we have assumed that the effective valences of the silver ion and iodine ion are $+0.6$ and -0.6, respectively, as inferred

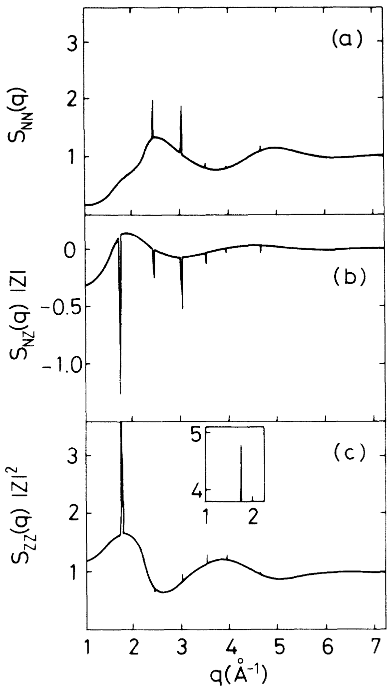

FIG. 1. (a) Number-number, (b) number-charge, and (c) charge-charge structure factors of α-AgI at $T = 170\,°\mathrm{C}$. The value of the effective valences are $|Z_{\mathrm{Ag}}| = |-Z_{\mathrm{I}}| \equiv |Z| = 0.6$.

from the phonon-dispersion measurement.[11]

Knowing the charge-charge structure factor, the dielectric function may be obtained from Eq. (2). The value of the equilibrium number density has been determined from the lattice-parameter measurement performed by Hoshino.[9] The wave-number–dependent static dielectric function is shown in Fig. 2. From Eq. (2), the fact that the structure factor is positive tells us that $\varepsilon(q) > 1$ or $\varepsilon(q) < 0$. If these conditions are violated, the system is unstable against charge-density-wave formation.[12] In our case, the static dielectric function changes sign at $q = 2.45$, 3.02, 3.53, 3.96, and 4.67 Å^{-1}, which correspond to the positions of the Debye lines in reciprocal space.[10] These peaks are interpreted as evidence of the rigid iodine sublattice. It is interesting to note that the contribution of the peak at $q = 1.76$ Å^{-1} in $S_{ZZ}(q)$ to $\varepsilon(q)$ is insignificant. The authors do not understand whether this behavior is merely a numerical effect, or has a more profound physical meaning. Although the main conclusions which we arrive at are unaffected, we ignore the experimental error bars in our analysis. Thus, the above behavior at $q = 1.76$ Å^{-1} may be due to this fact.

The smooth part of the dielectric function shown in Fig. 2 comes from the diffuse scattering. Its behavior resembles the dielectric function of the strongly coupled one-component plasma obtained by Fasolino, Parrinello, and Tosi,[13] which is shown in Fig. 4. This resemblance reflects the nearly liquidlike motion of the silver ions within the material. The smooth component of the dielectric function changes sign at $q \simeq 7.3$ Å^{-1}. A similar behavior has been obtained in the molecular-dynamics simulation of hydrogen plasma.[14]

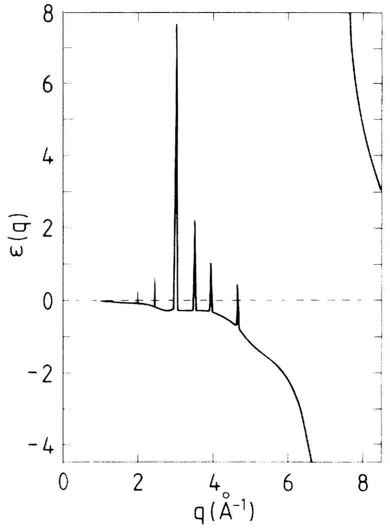

FIG. 2. Ionic component of the static dielectric function of α-AgI determined from the structural analysis data.

Normally, the polarizability of a material consists of three parts: electronic, ionic, and dipolar. The dielectric function discussed above arises mainly from the contribution of ionic polarizability, that is, from the displacement of one ion with respect to others.

An expression for the electronic part of the wave-number–dependent dielectric function has been derived by Penn.[3] His dielectric function can be plotted by an approximate interpolation formula,

$$\varepsilon_{\mathrm{el}}(q) = 1 + \left(\frac{h\omega_p}{E_g}\right)^2 F\left[1 + \left(\frac{E_F}{E_g}\right)\left(\frac{q}{k_F}\right)^2 F^{1/2}\right]^{-2}, \quad (4)$$

where

$$F = 1 - \left(\frac{E_g}{4E_F}\right) + \frac{1}{3}\left(\frac{E_g}{4E_F}\right)^2, \quad (5)$$

$\omega_p = (4\pi N e^2/m)^{1/2}$ is the plasma frequency, and E_F and k_F are the Fermi energy and wave number, respectively. E_g is treated as an adjustable parameter to be determined by experiment. Although the Penn model is strictly valid for semiconductors, the expression shown in Eq. (4) seems to give reasonable results for insulators too.[6] The electronic dielectric function of α-AgI evaluated by using Penn's formula is shown in Fig. 3. We have assumed four valence electrons as in semiconductors. E_g has been determined by equating $\varepsilon_{\mathrm{el}}(0)$ to $\varepsilon_\infty = 4.8$.[15] The total dielectric function of α-AgI is given by the summation of its ionic and electronic parts. In Fig. 3, the electronic static dielectric function of β-AgI, Si,[4] GaAs,[4] and KCl[5] are also shown for comparison.

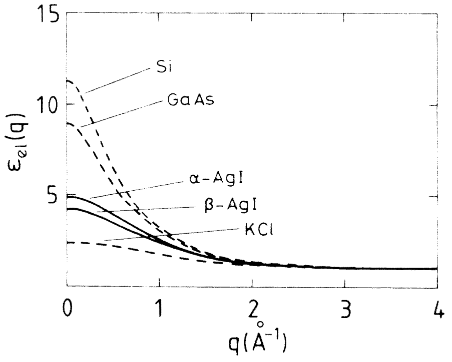

FIG. 3. Electronic component of the static dielectric function of α-AgI and β-AgI. The dielectric functions of Si (Ref. 4), GaAs (Ref. 4), and KCl (Ref. 5) are also shown for comparison.

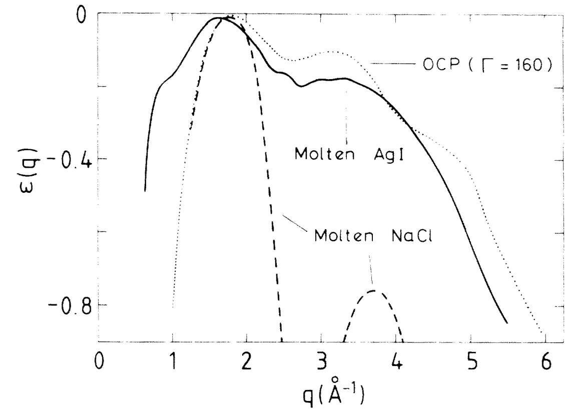

FIG. 4. Ionic component of the dielectric function of molten AgI, molten NaCl (Ref. 13), and one-component plasma (Ref. 13).

The dielectric function of β-AgI shown in Fig. 3 has been evaluated by using Penn's formula, but now, by equating $\varepsilon_{\mathrm{el}}(0)$ to $\varepsilon_\infty=4.2$.[16] In β-AgI all the ions are oscillating around their lattice points. The measured static dielectric constant of β-AgI, which is $\varepsilon_0=7.0$,[17] contains both electronic and lattice-vibrational or ionic-polarization contributions.

The halides and chalcogenides of silver and copper compounds show behaviors intermediate between solid and liquid in many of their physical properties. Therefore, it will be interesting to compare the dielectric function in these two phases. The dielectric function of molten AgI, which is evaluated by using Eq. (2), is shown in Fig. 4. For the charge-charge structure factor we have used the result of hypernetted-chain calculations performed by Stafford and Silbert[18] at $T=873$ K. In Fig. 4 the static dielectric functions of molten NaCl and the one-component plasma with plasma parameter $\Gamma=160$ are also shown.[13] According to Slattery, Doolen, and DeWitt, the fluid-solid transition of a classical one-component plasma takes place at $\Gamma\simeq168$.[2,19] It is interesting to note that the dielectric function of molten AgI resembles more closely that of the strongly coupled plasma near the fluid-solid transition than that of the molten salt NaCl. The authors speculate that this behavior reflects the covalent nature of AgI[20] and the tendency of the ions in the molten phase to take the structure of α-AgI. This observation must be complemented with our recent suggestion that the superionic phase can be described by a liquidlike picture.[21,22]

In conclusion, in this Letter we report the first comparative study of the static dielectric function of AgI in its β, α, and molten phases. Overall we have found that the ionic part of the dielectric function of α-AgI indicates the existence of a static charge-density wave, which reflects the iodine sublattice. We also have found that the dielectric function in the molten phase resembles that of the strongly coupled one-component plasma near its fluid-solid transition. To finalize, we mention that $\varepsilon(q)$ may have many applications.[4] For instance, it may be used to calculate the lattice vibration spectrum, to determine the screened pseudopotential form factor, etc.

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