

### Low-temperature dielectric properties of KI:Ag<sup>+</sup>: Additional evidence for the coexistence of two elastic configurations

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The observation of an anomalous temperature dependence in the dielectric constant of KI:Ag<sup>+</sup> at low temperatures supports the hypothesis that two elastic configurations coexist for this defect-lattice system.

The unusual temperature-dependent behavior of the far-infrared impurity-induced absorption spectrum for KI:Ag<sup>+</sup> has led to the conjecture that two inequivalent elastic configurations are simultaneously available to the defect-lattice system. Furthermore, it has been proposed that the low-energy configuration corresponds to on-center behavior of the Ag<sup>+</sup> ion and that the high-energy configuration, to off-center behavior.<sup>1</sup> In this Rapid Communication we describe our investigation of the temperature-dependent dielectric constant of KI:Ag<sup>+</sup>. The results are compared to and contrasted with those for RbCl:Ag<sup>+</sup> which is known to be off center at low temperatures. Our measurements directly show that the Ag<sup>+</sup> ion in KI is off center in the configuration which is populated at elevated temperatures.

Low-temperature dielectric constant measurements often have been used to identify the reorientation of dipolar defects in solids.<sup>2,3</sup> The Clausius-Mossotti equation for a medium with intrinsic dielectric constant  $\epsilon_0$  which contains  $N_i$  polarizable defects per cm<sup>3</sup> is

$$\frac{\bar{\epsilon} - 1}{\bar{\epsilon} + 2} = \frac{\epsilon_0 + \tilde{\Delta} - 1}{\epsilon_0 + \tilde{\Delta} + 2} = \frac{\epsilon_0 - 1}{\epsilon_0 + 2} + \frac{4\pi N_i \tilde{\alpha}_i}{3}, \quad (1)$$

where  $\tilde{\Delta}$  is the defect-induced contribution to the complex dielectric constant and  $\tilde{\alpha}_i$  the dipolar polarizability of the defect. Solving Eq. (1), in the limit of small  $N_i$ , one obtains for the impurity-induced dielectric constant

$$\tilde{\Delta} = 4\pi N_i \tilde{\alpha}_i \left( \frac{\epsilon_0 + 2}{3} \right)^2. \quad (2)$$

In the classical Debye relaxation approximation when the thermal energy is much larger than the reorientational energy level spacings, the dielectric response at frequency  $\omega$ , is

$$\Delta_1 + i\Delta_2 = \Delta_0 (1 - i\omega\tau)^{-1}, \quad (3)$$

where

$$\Delta_0 = 4\pi N_i \left( \frac{p^2}{3kT} \right) \left( \frac{\epsilon_0 + 2}{3} \right)^2, \quad (4)$$

$p$  is the dipole moment,  $k$  Boltzmann's constant,  $T$  temperature, and  $\tau$  the relaxation time.

At low temperature the Ag<sup>+</sup> ion is off center in the  $\langle 110 \rangle$  directions in RbCl with a tunnel splitting<sup>4</sup> of  $\sim 0.1$  GHz. By varying temperature at a fixed frequency the system can be swept from  $\omega\tau \gg 1$  to  $\omega\tau \ll 1$  and the resultant dielectric properties compared with the predictions of Eq. (3). Measurement of the temperature dependence of the dielectric constant has been used both to determine how

$\tau$  decreases with increasing  $T$  and to identify the dipole moment associated with reorientation of the Ag<sup>+</sup> in this host<sup>4,5</sup> ( $p = 4.3 \pm 0.3$  D). There is some value in contrasting the temperature-dependent signature characteristic of this standard off-center system with the KI:Ag<sup>+</sup> results.

Two kinds of samples have been studied in our dielectric measurements: pressed pellets of quenched polycrystalline material and Czochralski grown single crystals. (1-mm-thick by 1.2-cm-diam samples of both types were studied.) Sample electrodes were formed by first evaporating a thin layer of Cr and then a thick layer of In onto two surfaces. The sample was held in place by a pair of spring-loaded brass cylinders which pressed against the indium electrodes to ensure good electrical contact between the sample and the capacitance bridge circuit. The sample holder which could be heated electrically was surrounded by a vacuum chamber and the entire assembly was immersed in liquid helium. The thermal contact between the sample and the liquid-helium reservoir was controlled with helium exchange gas and the sample temperature was monitored with a calibrated carbon resistor attached to one of the brass cylinders.

The temperature-dependent dielectric properties of both kinds of RbCl:Ag<sup>+</sup> samples are similar: Concomitant with a change in  $\epsilon_1$  is a change in  $\epsilon_2$  of similar magnitude. The

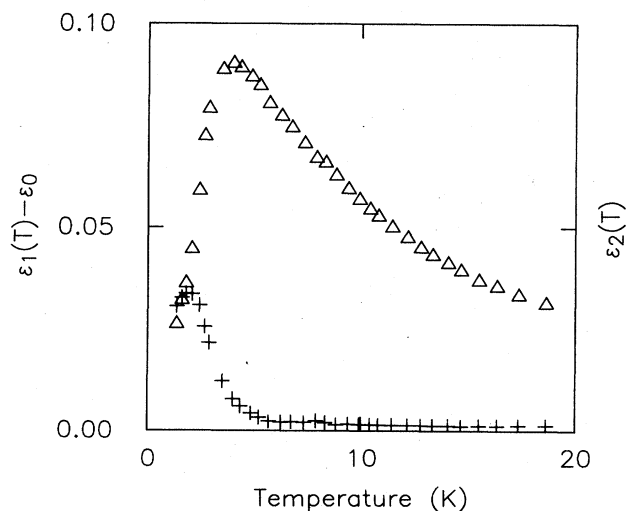


FIG. 1. Temperature dependence of the impurity-induced dielectric constant for RbCl:Ag<sup>+</sup>. Both  $[\epsilon_1(T) - \epsilon_0(1.4 \text{ K})]$  (the triangles) and  $\epsilon_2(T)$  (the crosses) are plotted vs temperature for a pressed polycrystalline sample of RbCl doped with 0.5% AgCl in the melt. The measuring frequency is 10 kHz.

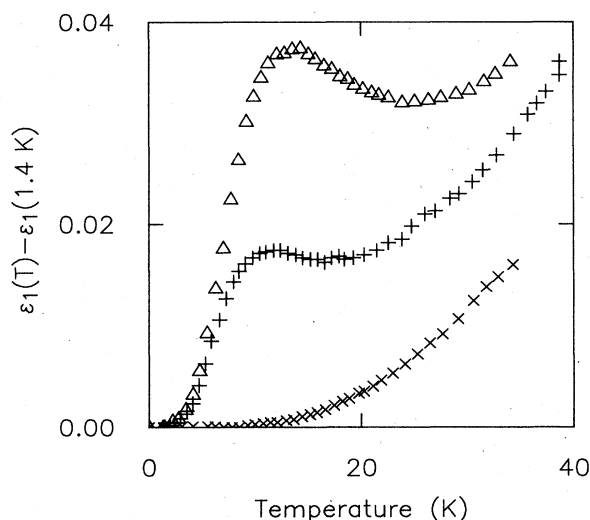


FIG. 2. Temperature dependence of the impurity-induced dielectric constant for KI:Ag<sup>+</sup>.  $\epsilon_1(T) - \epsilon_1(1.4 \text{ K})$  is plotted vs temperature for single-crystal samples of 0.5 and 0.2 mole% AgI in KI in the melt (the triangles and crosses, respectively). Also shown is the temperature dependence of  $\epsilon_0(T) - \epsilon_0(1.4 \text{ K})$  for pure KI (the  $\times$ 's).  $\epsilon_2(T)$  is temperature independent and the same value for all three samples ( $\sim 1.5 \times 10^{-3}$ ). The measuring frequency is 10 kHz.

measured temperature dependence of  $\epsilon(T) - \epsilon_0(1.4 \text{ K})$  for the quenched polycrystalline sample is shown in Fig. 1. At 10-kHz frequency a Debye loss peak in  $\epsilon_2(T)$  is observed at  $T = 1.9 \text{ K}$ . As expected the position of this peak depends on the exciting frequency. At these low temperatures  $\epsilon_0(T)$  is temperature independent so that the magnitudes<sup>6</sup> in Fig. 1 are directly related to  $\Delta_1$  and  $\Delta_2$ . The peak in  $\epsilon_2(T)$  indicates that the relaxation rate must vary faster than linearly with  $T$  and the high-temperature data ( $\omega\tau \ll 1$ ) for the real part give  $N_i(\text{Ag}^+) \approx 2.7 \times 10^{18} \text{ cm}^{-3}$ . The single-crystal data are in agreement with previously reported results.<sup>4,5</sup> The real part is similar to that shown in Fig. 1 but at the lowest temperatures the imaginary part increases monotonically as temperature decreases indicating that the relaxation rate varies linearly with temperature.

Our measurements of the temperature-dependent dielectric properties of KI:Ag<sup>+</sup> are shown in Fig. 2. Although  $\epsilon_1(T) - \epsilon_1(1.4 \text{ K})$  shows a maximum at about 12 K no corresponding loss peak is observed in  $\epsilon_2(T)$ ; moreover, the spectra shown in Fig. 2 are independent of the excitation frequency. Both of these results indicate that  $\omega\tau \ll 1$  over the entire temperature range of our measurements. Equations (3) and (4) show that in this limit  $\Delta_1 = \Delta_0 \alpha N_i(T)/T$  so that the temperature-dependent measurement of the real part of the dielectric constant provides a direct determination of the population in the off-center configuration.

To show the temperature dependence of the population in the second elastic configuration, the data in Fig. 2 for 0.5 mole% AgI-KI are subtracted from pure KI, the result multiplied by  $T$  and plotted versus temperature in Fig. 3. At high temperature the data points indicate that the off-center population levels off at a constant value. If the number density of off-center Ag<sup>+</sup> ions at high temperature is set equal to the number density of Ag<sup>+</sup> ions which produce resonant modes<sup>7</sup> in the crystal ( $1.3 \times 10^{18} \text{ cm}^{-3}$ ) then the calculated dipole moment is  $p = 1.8 \pm 0.4 \text{ D}$ .

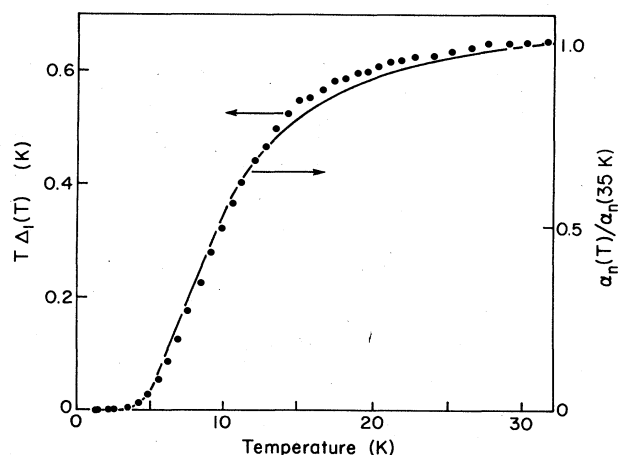


FIG. 3. Measured temperature dependence of  $T\Delta_1$  for KI:Ag<sup>+</sup>. This quantity is proportional to the population in the off-center configuration (dotted curve). The initial rise of the data with temperature follows an energy gap law with gap = 24 K. Also shown is the nonresonant far-infrared absorption coefficient for KI:Ag<sup>+</sup> at  $4 \text{ cm}^{-1}$ . It is normalized to its high-temperature value (solid curve).

An estimate of the energy separation between the on- and off-center configurations can be obtained by fitting the population in the off-center configuration to an energy gap law at low temperatures. This spacing is found to be  $24 \pm 2 \text{ K}$  independent of how rapidly the sample is quenched to helium temperature.

Information about the reorientational relaxation time for Ag<sup>+</sup> in KI can be obtained by combining the experimental results for the dipole moment from the dielectric constant measurement with the measured temperature dependence of the nonresonant absorption coefficient,  $\alpha_n$ , in the far-infrared spectral region.<sup>1</sup> The normalized value of  $\alpha_n$  at  $4 \text{ cm}^{-1}$  (the solid line) is plotted versus temperature in Fig. 3. According to Eq. (3), for the limit  $\omega\tau \gg 1$ , the absorption coefficient

$$\alpha_n = \frac{\Delta_0}{c\sqrt{\epsilon_0}} \left( \frac{1}{\tau} \right) \quad (5)$$

Since the experimental data follow  $N_i(T)$  and since Eq. (5) predicts that the data should vary as  $N_i(T)/[T\tau(T)]$ , we conclude that  $T\tau(T) = \text{const}$ . From the magnitude of the nonresonant absorption we find

$$\tau^{-1} = (3 \pm 1) \times 10^{10} (T) \text{ sec}^{-1}$$

A temperature dependence of this form is expected to occur when phonon-assisted tunneling is the dominant relaxation mechanism for the off-center ion.

The picture that emerges from our measurements is that two elastic configurations exist for this lattice-defect system. At low temperature the Ag<sup>+</sup> ion in KI is on center and resonant mode absorption is observed in the far infrared. When the temperature is increased a second elastic configuration which has an energy about 24 K above the ground state becomes populated. The large increase in the defect contribution to the dielectric constant indicates that the Ag<sup>+</sup> ion is off center in this second elastic state. Because the off-center population appears to approach a constant value

at elevated temperatures we conclude that only these two elastic configurations are close by in energy.

The  $\text{Ag}^+$  ion in  $\text{RbCl}$  may show a similar two-state behavior. From measurements of the paraelectric absorption spectrum as a function of hydrostatic pressure at helium temperature, Bridges and co-workers have concluded that two kinds of isolated  $\text{Ag}^+$  centers coexist near 1.35-K bars—an on- and an off-center one.<sup>8</sup> Far-infrared measure-

ments on this system as a function of hydrostatic pressure should be particularly rewarding.

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