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Observation of Two Elastic Configurations at a Point Defect

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The anomalous temperature dependence of the impurity-induced far-infrared spectrum of KI:Ag^+ indicates that at least two energetically inequivalent elastic configurations are simultaneously available to the defect-lattice system.

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With Kirby's seminal experimental work[1] in 1971 on the delineation of the gap and resonant modes for Ag^+ in KI, the vibrational properties of the point defect in solids appeared well understood. His observations confirmed to such a degree the original Lifshitz model,[2-4] where the impurity and the strained lattice are replaced by a molecular defect space embedded in a perfect lattice, that few measurements have been made on this or other simple defect systems since that time. In particular, the temperature-dependent properties of the complete impurity-induced spectrum never have been measured.

In this Letter we describe unexpected temperature dependences of the far-infrared spectrum of Ag^+ in KI. Most surprising is that the low-temperature vibrational absorption lines decrease in strength and new features with different characteristic frequencies grow as the temperature is increased from 1.2 to 10 K. In contrast with this unusual behavior in KI, the NaI:Ag^+ spectrum behaves normally with increased temperature, i.e., over the same temperature range no temperature dependence is observed. The experimental data for KI:Ag^+ can be understood if it is postulated that a new elastic configuration of the impurity-lattice system has an energy close to the ground-state value. This second configuration, with its own Ag^+-induced vibrational spectrum, becomes populated at elevated temperatures.

The Ag^+-induced absorption spectra in KI at two temperatures are shown in Fig. 1. The solid curve in Fig. 1(a) shows the impurity-induced absorption coefficient $\alpha(\omega)$ versus frequency at 1.2 K. This spectrum is the same as that reported earlier[1] and the assignments are identified in the figure caption.

The entire spectrum is very temperature dependent as shown by the dotted absorption curve for 10 K in Fig. 1(a). With increasing temperature the strengths of the resonant mode, combination bands, and local mode all decrease while a broad absorption band at high frequencies increases. This last effect is due to the intrinsic two-phonon difference processes and is identical to that observed in pure KI.

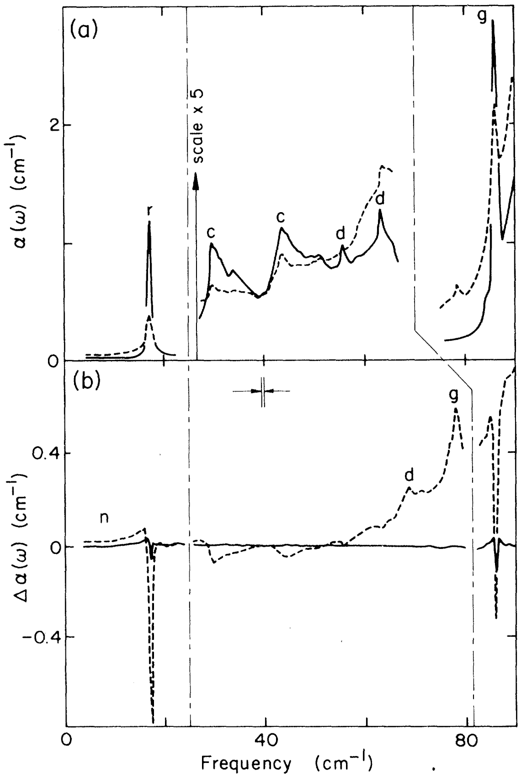

FIG. 1. Temperature dependence of the Ag^+-induced absorption spectrum in KI. The vertical dot-dashed lines divide the figure into three parts: The concentration in the center (2×10^{18} Ag^+/cm^3) is twice that of the end regions. Assignment of the different features: r = resonant mode, c = combination band, d = density of states, g = gap mode, and n = nonresonant absorption. (a) The absorption coefficient vs frequency for two temperatures: solid curve, 1.2 K; dashed curve, 10 K. (b) absorption coefficient difference between a given temperature and 1.2 K vs frequency for two temperatures: solid curve, 3.4 K; dashed curve, 10 K. Note that the ordinate in the center region of (a) is expanded 5 times.

Numerous low-temperature studies of the sharp absorption line at 17.3 cm^{-1} in KI:Ag^+ with uniaxial stress and electric field have demonstrated that the Ag^+ ion behaves as a substitutional impurity at a normal lattice site[5]; the impurity does not exhibit displacive tunneling nor is it frozen in an off-center position.

The temperature dependence of the absorption coefficient in the low-frequency region around the resonant mode is shown in Fig. 2. The decrease in the resonant-mode strength is accompanied by a corresponding increase in a broad absorption which appears to be nearly frequency independent from the smallest wave numbers measured (3 cm^{-1}) to at least 25 cm^{-1}. The magnitude of this nonresonant absorption is proportional to the low-temperature strength of the resonant mode over a factor of 40 in Ag^+ concentration.

There are other spectral features which appear at elevated temperatures as can be seen most easily in Fig. 1(b) where the difference in absorption coefficient $\Delta\alpha(\omega)$ between a given temperature and the 1.2-K reference is plotted versus frequency. The solid curve is for $T = 3.4$ K and the dashed one for 10 K. A positive $\Delta\alpha(\omega)$ in this figure indicates that the sample absorbs more at high temperatures than at 1.2 K and vice versa. In addition to the nonresonant absorption, *n*, at low frequencies there are two additional new impurity-induced features which appear at elevated temperatures, namely, a density-of-states peak, *d*, and a gap mode, *g*, at 69 cm^{-1} and 78.6 cm^{-1}, respectively. (Note that the KI gap extends from 70 to 96 cm^{-1}). All three of the absorptions have similar temperature dependencies: They are not observable at 1.2 K and grow in magnitude with increasing temperature. The common low-temperature behavior indicates that all of these absorptions probably have the same elevated ground-state energy (14 to 20 cm^{-1}).

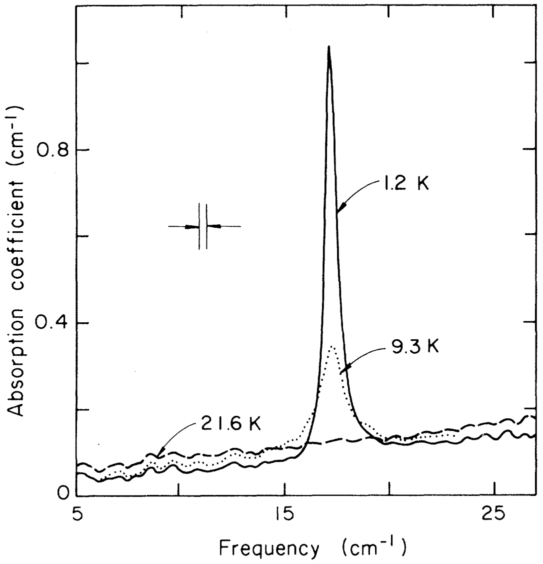

FIG. 2. Temperature dependence of the absorption spectrum of KI + 0.2 mole% AgI in the frequency region of the resonant mode. The three temperatures are identified in the figure. At high temperatures the broad nonresonant absorption coefficient is about 3% of the low-temperature resonant-mode peak value.

An important experimental finding is that the temperature dependences of the strengths of the two strong modes, labeled *r* and *g* in Fig. 1(a), are essentially the same. The strength $I(T)$ of the infrared-active resonant or gap mode at a particular temperature T is defined as

$$I(T) \equiv \int_{\text{line}} \alpha(\omega)\,d\omega, \tag{1}$$

where $\alpha(\omega)$ is the absorption coefficient at frequency ω. The temperature dependence of the measured strength $I(T)$ of each line is plotted in

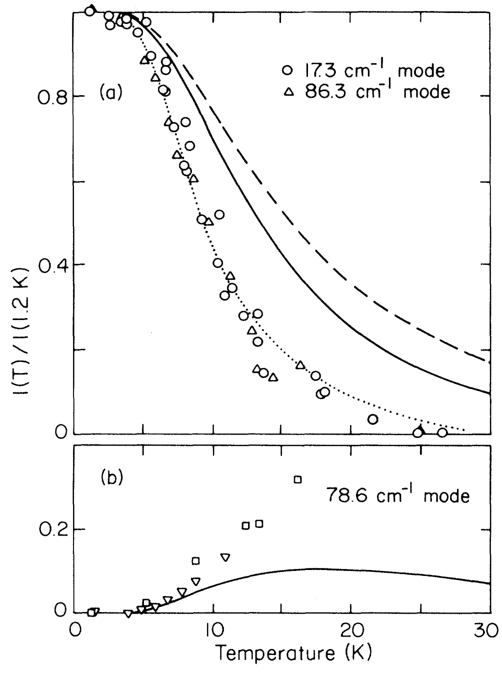

FIG. 3. Normalized absorption strength vs temperature for the resonant and gap modes in KI:AgI. (a) Ground-state gap and resonant-mode data for a number of Ag^+ concentrations. Solid and dashed curves are the predictions of the three-dimensional double anharmonic oscillator model. The dotted curve which is 1 minus the nonresonant growth curve data is taken at 4 cm^{-1}. (b) Excited-state gap mode data. The solid curve shows the predicted temperature dependence of the excited-state strength for the same anharmonic model as used in (a).

Fig. 3(a). The growth of the gap mode at 78.6 cm^{-1} is shown in Fig. 3(b). The strength of this mode is normalized to the low-temperature strength of the gap mode at 86.3 cm^{-1}.

It might appear that these temperature dependences could follow from simple population effects for anharmonic oscillators, but as we now show this is not the case. With excitation numbers labeled (g,r) for the three-dimensional double anharmonic oscillator, the calculated temperature dependences shown in Fig. 3 are as follows: $(0,0) \rightarrow (0,1)$ transition, solid line, and $(0,0) \rightarrow (1,0)$, dashed line in Fig. 3(a); and $(0,1) \rightarrow (1,1)$, solid line in Fig. 3(b). The temperature dependences associated with population effects are too slow to account for the data. In addition, at elevated temperatures the predicted $(0,1) \rightarrow (0,2)$ transition is not observed in Fig. 2.

A model that was thought to explain the temperature-dependent properties of ir-active resonant modes made use of linear coupling between them and other even resonant modes.[6] Not only is this predicted temperature dependence too weak to explain the data in Fig. 3, but also, and more convincingly, the experimental data in Fig. 1 show that with increasing temperature the strength is not transferred from the ir-active resonant mode, r, to the combination bands, c, as expected since the combination-band strengths disappear as well.

In order to understand better the role of the nonresonant absorption we have measured the temperature dependence of this contribution at a frequency far removed from the resonant-mode region. A broad-band millimeter-wave spectrum with an intensity maximum centered at 4 cm^{-1} and a full width at one-half peak height of 4 cm^{-1} was used to measure the nonresonant absorption growth curve. By subtraction of the normalized growth curve from unity, the data can be compared directly with the temperature dependence of the resonant- and gap-mode strengths. These data are represented by the dotted line in Fig. 3(a). Although it is not yet possible to make a quantitative statement it appears that most of the strength lost by the gap and resonant modes is transferred to the nonresonant absorption.

In contrast with the unusual temperature dependences observed for the KI:Ag^+ spectrum, no appreciable temperature dependence, besides the intrinsic difference-phonon processes, is found in the impurity-induced spectrum of NaI:Ag^+. In particular the strength of the T_{1u} resonant mode, which occurs at 36 cm^{-1}, is temperature independent up to the highest temperature measured (35 K).

These radically different experimental findings for the same impurity surrounded by the same nearest neighbors in two neighboring alkali halides make it highly unlikely that the lattice dynamics models used to date can describe the measured spectra of both of these impurity systems. To account for the experimental data we propose that under certain circumstances a second elastic configuration can occur in addition to the ground-state arrangement of the defect-lattice system. The rapid temperature dependences observed for KI:Ag^+ require that the second configuration must contain a low-lying multiplet with a large degeneracy, perhaps related to displacive tunneling of the Ag^+ defect among many equivalent minima centered about a normal lattice site. (A twelve-component spectrum with a tunneling splitting of ~ 0.1 cm^{-1} has been identified[7] for the normal ground-state configuration of Ag^+ in RbCl). As long as the thermal and electromagnetic energies are much larger than the tunnel splitting, the frequency dependence of the absorption coefficient for such an arrangement is expected to have the Debye form,[7] namely,

$$\alpha_n = \frac{4\pi N p^2}{3kT} \frac{\omega^2 \tau}{nc(1+\omega^2\tau^2)}, \tag{2}$$

where N is the number of off-center Ag^+ ions, p is the effective dipole moment, and the phonon-assisted tunneling relaxation time is $\tau \sim (T)^{-1}$. In the limit where $\omega\tau >> 1$, α_n is frequency independent and gives a direct measure of the temperature dependence of N. The fact that $1 - N(T)/N(35\ \mathrm{K})$ follows the temperature dependence of the resonant- and gap-mode strengths [Fig. (3a)] is strong evidence for the existence of two configurations.

The large difference in the temperature-dependent properties of Ag^+ in NaI and KI leads us to speculate that additional low-lying configurations can only occur when the impurity ion is smaller than the host ion it replaces ($\mathrm{Na}^+ < \mathrm{Ag}^+ < \mathrm{K}^+ < \mathrm{Rb}^+$). This conjecture is supported by hydrostatic pressure measurements[8] which have been used to transform off-center systems such as RbCl:Ag^+ to on-center ones. The almost discontinuous change observed[8,9] in the impurity ion position at low temperature and finite pressure would be a natural consequence if two different elastic configurations could exist simultaneously for the defect-lattice system. The apparent transition would occur whenever the pressure-tuned ground states of two configurations have the same energy so that direct configurational tunneling becomes possible.

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[1] R. D. Kirby, Phys. Rev. Lett. **26**, 512 (1971), and Phys. Rev. B **4**, 3557 (1971).

[2] I. M. Lifshitz, Nuovo Cimento Suppl. **3**, 716 (1956).

[3] A. A. Maradudin, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1966), Vols. 18 and 19.

[4] M. V. Klein, in *Physics of Color Centers,* edited by W. Beall Fowler (Academic, New York, 1968), p. 429.

[5] A. S. Barker and A. J. Sievers, Rev. Mod. Phys. **47**, S-2 (1975), Chap. 6.

[6] R. W. Alexander, A. E. Hughes, and A. J. Sievers, Phys. Rev. B **1**, 1563 (1970).

[7] H. Fröhlich, *Theory of Dielectrics* (Oxford Univ. Press, London, 1949), p. 70.

[8] U. Holland and F. Lüty, Phys. Rev. B **19**, 4298 (1979).

[9] R. P. Devaty and A. J. Sievers, Phys. Rev. B **22**, 4074 (1980).