PHYSICAL REVIEW B VOLUME 6, NUMBER 2 15 JULY 1972

Resonant Phonon Modes of Ag^+ and Au^+ in Alkali Halides

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(Received 17 November 1971)

Band-model calculations of resonant modes due to Ag^+ impurity in sodium halides and Au^+ impurity in sodium and potassium halides have been made in the isotopic-mass-defect approximation of Brout using a model density of phonon states. The results are compared with available experimental data. Good agreement is obtained for the Ag^+ resonances in sodium halides. The Au^+ resonant modes in NaCl, NaBr, and NaI are predicted at 38, 26, and 19 cm^{-1}, respectively. The Au^+ low-frequency resonances in KCl, KBr, and KI are predicted at 25.2, 19.8, and 10.6 cm^{-1}, respectively. This estimate includes the softening of the modes due to changes in the force constant near the impurity. The high-frequency resonant modes of Au^+ in KCl and KBr show good agreement with the experimentally observed Raman modes at 61 and 58 cm^{-1}, respectively. The problem of the Ag^+ resonances in potassium halides remains unsolved in our model.

I. INTRODUCTION

Defect vibrational modes in crystals have been studied at length[1] since first theoretically predicted by Lifshitz.[2] The effect of introducing impurities is to produce two types of modes depending upon the nature of the impurity. First, there are discrete (localized or gap) modes produced outside the band of perfect-lattice frequencies. Second, there are resonant (band) modes which lie within the band of lattice frequencies. Localized modes have frequencies larger than that of the highest LO mode of the lattice, while the gap modes have frequencies which lie in the gap of the acoustic and optical branches of the host crystal. For both these modes the vibrational amplitudes fall off exponentially with increasing distance from the impurity, i.e., the modes are spatially localized in character. Resonant modes, on the other hand, have vibrational amplitudes which, though peaked at the resonant frequencies, do not fall off as rapidly as those of the localized modes.

Theoretical models of defect vibrational modes in crystals fall into two broad categories: band model[2,3] and molecular model.[4] The band model utilizes the density of phonon states of the pure crystal in calculating impurity modes and, as such, both localized and resonant modes are treated on an equal footing. The molecular model, on the other hand, treats the impurity and its nearest neighbors as a vibrating molecule, precluding the possibility of resonant modes.

In this paper we present band-model calculations of the resonant mode frequencies of an Ag^+ impurity in sodium halides and an Au^+ impurity in sodium and potassium halides. In evaluating the frequencies, a model density of phonon states[5] is used for the host lattice. Its properties and the method of evaluating the mode frequencies in the isotopic-mass-defect approximation[3] (IMDA) is given by Sec. II. Section III discusses the determination of the "effective force constant" in analogy with the F-center model.[6] The effect of including the force-constant change is to soften the mode frequencies of Sec. II. Results of these calculations and comparison with experimental data are discussed in Sec. IV.

II. CALCULATION OF UNSOFTENED MODE FREQUENCIES

When an impurity atom goes into a perfect-lattice site, three distinct changes are produced in the neighborhood of the impurity: mass, force-constant, and charge defects.[7] Any theoretical model which attempts a calculation of the impurity vibration frequencies should incorporate three defect parameters Δm, f^*, and e^* characterizing the mass, force-constant, and charge defects, respectively. For the simplest approximation, i.e., isotopic-mass-defect approximation, charge and force-constant defects are neglected. In this case, the vibrational frequencies of a substitutional impurity are given by the solution of[3]

$$D(\omega) = 1 + \frac{\Delta m}{mN} \sum_{\vec{q}} \frac{\omega^2}{\omega^2 - \omega_{\vec{q}}^2} = 0 , \quad (1)$$

where $\Delta m = m' - m$, with m' being the impurity mass and m the mass of the substituted ion. The summation is over all phonon modes of the host lattice, whose density of states $\nu(\omega)$ is normalized such that

$$\int_0^{\omega_m} \nu(\omega)\, d\omega = 1 . \quad (2)$$

Equation (1) may also be written

$$D(\omega) = 1 + \epsilon \omega^2 \mathcal{P} \int_0^{\omega_m} \frac{\nu(\omega')\, d\omega'}{\omega^2 - \omega'^2} = 0 , \quad (3)$$

where ϵ is the mass defect $\Delta m/m$, $\nu(\omega)$ is the normalized density of states, ω_m is the maximum lattice frequency, and the principal value of the

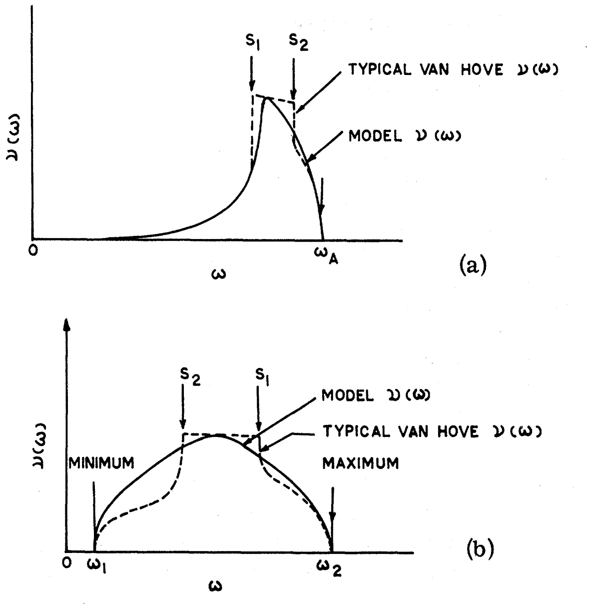

FIG. 1. (a) The dashed curve gives the van Hove density of states for an acoustic-like branch, while the solid curve is the model density of states. (b) The dashed curve gives the van Hove density of states for an optical-like branch, while the solid curve is the model density of states.

integral is required. The width of the resonant mode at ω_0 is given by[3]

$$\tfrac{1}{2}\Gamma = \left| \frac{\operatorname{Im} D(\omega + i\epsilon)}{\operatorname{Re} D'(\omega)} \right|_{\omega=\omega_0} . \tag{4}$$

The model $\nu(\omega)$ for the host lattice consists of four different $\nu_i(\omega)$ corresponding to the LA, TA, LO, and TO branches. For the acoustic branches

$$\nu_A(\omega)\,d\omega = \alpha\omega^2(\omega_A - \omega)^{1/2} d\omega \ , \tag{5}$$

ω_A being the cutoff frequency and α the normalization factor. Similarly, for the optic branches

$$\nu_0(\omega)\,d\omega = \alpha'(\omega - \omega_1)^{1/2}(\omega_2 - \omega)^{1/2} d\omega \ , \tag{6}$$

where ω_1 and ω_2 are the lower- and higher-frequency cutoffs. The $\nu(\omega)$ are schematically given in Fig. 1.

This model density of states[5] incorporates the correct M-type (maxima and minima) van Hove singularities[8] while smearing out those of the S type (saddle points).

Our model $\nu(\omega)$ have been fitted in the different branches to the $\nu(\omega)$ of Karo and Hardy[9] to obtain the frequency cutoffs. These are given in Table I. The resonant frequencies ω_0 and the widths $\frac{1}{2}\Gamma$ were determined by solving Eqs. (3) and (4) numerically on an ICL 1909 computer. For a given impurity two resonance modes are obtained for any crystal: The low-frequency mode is acoustic-phonon-like in character, while the high-frequency one is optic-phonon-like. The results of calculations of Ag⁺ resonant modes in sodium halides and Au⁺ resonant modes in sodium and potassium halides are given in Tables II–IV. These tables also contain values of ϵ_m, the minimum mass defect necessary to obtain a low-frequency resonance in these crystals.

The widths $\frac{1}{2}\Gamma$ determined by Eq. (4) are found to be fairly good for the modes obtained in the near acoustic region but not for those obtained in the near optic region. This is probably because the modes obtained in the near optic region generally occur at the low-energy shoulder of the model $\nu(\omega)$ where $\operatorname{Re} D(\omega)$ varies very rapidly. In this case, the width $\frac{1}{2}\Gamma$ is not correctly given by Eq. (4). The low-energy acoustic resonance, on the other hand, occurs in a region where the $\operatorname{Re} D(\omega)$ is slowly varying, and then Eq. (4) becomes appropriate.

III. DETERMINATION OF EFFECTIVE FORCE CONSTANT

The effective force constant coupling the impurity to its neighbors can be determined in the molecular model.[6] Neglecting the deformation of the positive ion, the force-constant softening is estimated from the two sets of Kellermann constants A_1, B_1 for the host lattice and A_2, B_2 for the impurity site. The force constants for the pure (f_1) and impure (f_2) lattices are given by

$$f_1 = A_1 + 2B_1 - (32\pi^2\alpha/qV_a)Z^2 \tag{7}$$

and

$$f_2 = A_2 + 2B_2 - (32\pi^2\alpha/qV_a)Z^2 \ . \tag{8}$$

Here V_a is the unit-cell volume $2r_0^3$, with r_0 being the equilibrium lattice constant, Z is the Szigetti effective charge e^*/e, and α is the polarizability given by the Clausius-Mossotti formula

$$\alpha = \frac{3V_a}{4\pi}\left(\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\right) , \tag{9}$$

where ϵ_∞ is the high-frequency dielectric constant. Assuming no relaxation of the lattice around the impurity, Eqs. (7) and (8) are simplified because

$$B_1 = B_2 = -\tfrac{2}{3} Z^2 \alpha_M \ , \tag{10}$$

where α_M is the Madelung constant. The constants A_1 and Z are evaluated by using the $\vec{k} \sim 0$ LO- and

TABLE I. Cutoff frequencies in units of wave numbers for the various phonon branches obtained from $\gamma(\omega)$ of Karo and Hardy (Ref. 9).

Crystal	ω_A(TA) (cm^{-1})	ω_A(LA) (cm^{-1})	ω_1(TO) (cm^{-1})	ω_2(TO) (cm^{-1})	ω_1(LO) (cm^{-1})	ω_2(LO) (cm^{-1})
NaCl	133	186	164	212	186	264
NaBr	91	106	112	191	184	223
NaI	63	76	95	148	127	196
KCl	111	159	111	153	138	214
KBr	76	106	85	127	116	170
KI	52	69	95	124	106	143

TABLE II. Resonant modes for Ag^+ impurity in sodium halides. The mass defect ϵ is 3.69.

Crystal	Minimum mass defect ϵ_m	Calculated resonance modes (cm^{-1})		Width $\frac{1}{2}\Gamma$ (cm^{-1})	Reported resonance modes[a] (cm^{-1})
		(low)	(high)	(low)	
NaCl	3.45	55	154	24.5	52.5
NaBr	3.62	43	114	16.6	48.0
NaI	3.67	32	95	12.7	36.7

[a] See Ref. 11.

TO-phonon frequencies[10] in

$$\mu V_a \omega_{\mathrm{LO}}^2 / e^2 = f_1 + \tfrac{8}{3}\pi Z^2 , \tag{11}$$

$$\mu V_a \omega_{\mathrm{TO}}^2 / e^2 = f_1 - \tfrac{4}{3}\pi Z^2 , \tag{12}$$

where μ is the reduced mass and ω_{LO} and ω_{TO} are the LO- and TO-phonon frequencies. To find A_2, the experimental infrared frequency has been matched with the highest F_{1u} eigenfrequency in Eq. (11),[6] with appropriate changes for μ. This procedure determines f_1 and f_2; the values of the force-constant softening for Au^+ in potassium halides is given in Table IV. The effect of the force-constant softening, which takes into account the change in the elastic binding coefficients, is to reduce the resonant frequencies. These are then obtained from the resonant frequencies in the IMDA by multiplying with the softening factor $(f_2/f_1)^{1/2}$, and the results are given in Table IV.

IV. DISCUSSION AND CONCLUSION

The resonant mode frequencies of Ag^+ impurity in sodium halides in the IMDA are given in Table II. It is seen that the calculated frequencies corresponding to acoustic-phonon-like modes agree well with the observed ones. In the same approximation, we predict the low-frequency resonant modes of Au^+ in NaCl, NaBr, and NaI at 38, 26, and 19 cm^{-1}, respectively, in Table III. It is expected that the IMDA will also be adequate for Au^+ resonance, since the mass defect ϵ is 7.56. This is much bigger than the minimum value for the mass defect ϵ_m, which is obtained for our model $\nu(\omega)$ in Eq. (3). For impurities with below this value no low-frequency resonances are obtained. The ϵ_m for low-frequency acoustic resonance in sodium halides ranges from 3.45 to 3.67.

The IMDA does not give resonant modes for Ag^+ in potassium halides. The value of ϵ in this case is 1.77, while ϵ_m ranges from 3.3 to 4. This result indicates that for heavier alkali halides the IMDA is inadequate and that changes in the force constant due to the impurity must be taken into account. This approach may be exemplified by considering the Au^+ resonances in potassium halides. In this case the IMDA gives resonance frequencies which, when softened as discussed in Sec. III, predict low-frequency modes at 25.2, 19.8, and 10.6 cm^{-1} for KCl, KBr, and KI, respectively. The prediction is made plausible by scaling the experimental value for the Ag^+ resonance in potassium halides by the square root of the ratio of the masses of Ag^+ and Au^+, $(M_{\mathrm{Ag}}/M_{\mathrm{Au}})^{1/2}$, and comparing with the calculated softened resonant frequencies for Au^+. Table IV shows that there is good agreement between the experimental and theoretical frequencies. The above procedure treats the Au^+ and Ag^+ in potassium halides as if they were isotopes of each other. This may be a good approximation, since the force-constant softenings for Au^+ in KCl, KBr, and KI (35.4, 35.8, and 25.8%, respectively) are comparable to the force-constant softening for Ag^+ in these crystals[11] (30.6, 36.0, and 17.2%, respectively).

Paucity of experimental data of the optic-phonon-like high-frequency resonant modes prevents detailed verification of our theoretical results. However, high-frequency resonant modes have been measured by Raman scattering for Au^+ in KCl, KBr, and KI at 58, 61, and 57 cm^{-1}, respectively.[12] The comparison between these and our calculations are made in Table III. Good agreement is found for Au^+ resonance in KBr and KCl. For Au^+ resonance in KI, a gap mode is obtained theoretically. This is to be expected, since ϵ is approximately equal to ϵ_m.

We conclude by stating that the resonant frequencies of Au^+ and Ag^+ in sodium halides are adequately treated in the IMDA. For potassium halides the

TABLE III. Resonant modes for Au^+ impurity in sodium halides. The mass defect ϵ is 7.56.

Crystal	Minimum mass defect ϵ_m	Calculated resonance modes (cm^{-1})		Width $\frac{1}{2}\Gamma$ (cm^{-1})
		(low)	(high)	(low)
NaCl	3.45	38	151	12
NaBr	3.62	26	111	3
NaI	3.67	19	92	6.3

TABLE IV. Resonant modes for Au^+ impurity in potassium halides. The mass defect ϵ is 4.1.

Crystal	Minimum mass defect ϵ_m	Calculated unsoftened resonance modes (cm^{-1}) (low)	(high)	Kellermann constants A_1	A_2	Force constant softening[a] (f_2/f_1) %	Softened modes $\omega_0(f_2/f_1)^{1/2}$ (cm^{-1}) (low)	(high)	Width $\frac{1}{2}\Gamma$ (cm^{-1}) (low)	Reduced infrared modes[b] (cm^{-1})	Raman modes[c] (cm^{-1})
KCl	3.31	42	109	12.34	6.36	35.48	25.2	65	6.6	28.5	61
KBr	3.95	33	85	12.45	6.94	35.83	19.8	51	6.5	25	58
KI	4	21	87	12.95	6.36	25.78	10.6	44.2	3.8	13	57

[a] The force-constant softenings obtained for Au^+ substitution are comparable to those for Ag^+ in these crystals (30, 36, and 17.2%, respectively). See Ref. 11, p. 475.

[b] These modes have been deduced from the ir data available for Ag^+ substitution in these crystals, assuming Au^+ to be an isotope of Ag^+. See Ref. 10, p. 475.

[c] See Ref. 12.

situation is different and force-constant changes due to the introduction of the impurity must be included. When this is done, the Au^+ resonances are satisfactorily explained. The problem of Ag^+ resonances in potassium halides remains unsolved in this paper.

ACKNOWLEDGMENTS

We wish to thank Dr. A. V. R. Warrier for helpful discussions. One of the authors (A. K. P.) gratefully acknowledges financial assistance from the CSIR, New Delhi, to this work.

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PHYSICAL REVIEW B VOLUME 6, NUMBER 2 15 JULY 1972

Dielectric Susceptibility of CN^- Ions in RbCl from 1 to 26 GHz*

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(Received 22 February 1972)

The real and imaginary parts of the dielectric susceptibility of the RbCl: CN^- system are measured throughout the 1–26 GHz range. The results, which show a relatively sharp absorption peak at 9.6 GHz and a smaller, broader peak at 4.5 GHz, agree with a model in which the CN^- rotation is both hindered by eight deep potential minima in the [111] directions (XY-8), and severely perturbed by the internal stresses of the crystal (these stresses producing the broad peak at 4.5 GHz). Such an interpretation, in addition to agreeing with the symmetry predictions of previous ultrasonic measurements, can also qualitatively explain the heretofore contradictory results of several other experiments.

INTRODUCTION

Of all the work done on the tunneling properties of substitutional impurities in alkali halide crystals,[1] only one system, KCl: Li^+, has to date consistently lent itself to a simple theoretical interpretation (that of the tunneling model of Gomez *et al.*[2]). It now appears, however, that the properties of another complex, RbCl: CN^-, may, with modifications due to the random strains within the