F-Center Gap Mode in Alakli Halides. A Molecular Model*

R. S. Singh and S. S. Mitra
Department of Electrical Engineering, The University of Rhode Island, Kingston, Rhode Island 02881
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A molecular model of the F center treated as a vibrating system enables one to explain the occurrence of an infrared-active gap mode associated with the center.

I. INTRODUCTION

An infrared-active gap mode associated with the F center in the KI has recently been reported.[1] We propose to predict the position and the intensity of the gap mode from a simple molecular model of the F center. According to the DeBoer model, the F center is an electron trapped at a vacant negative-ion site in an alkali halide crystal. Its first electronic transition observed in the visible region as a broad band for most alkali halides is known as the F band. Rosenstock and Klick[2] treated the F-center absorption as a vibrational problem due to the localized mode of oscillation of the F-center electron. Although this model gave a reasonable value for the absorption energy, it suffers from the following limitations: (i) The alkali halide crystal was approximated by a one-dimensional diatomic chain; (ii) the long-range Coulomb forces were ignored; and (iii) instead of a quantum-mechanical system the F-center electron and its immediate neighbors were treated as a classical normal mode problem. The local mode due to a U center (H^- or D^- substitutional imputity), also treated similarly, yielded good agreement with the experimental results.[3]

The molecular model of a point defect was first proposed by Jaswal[4] for the local mode due to U centers in alkali halides of the NaCl structure. In this model, the ions were treated rigid and the impurity ion and its six nearest neighbors were treated as a vibrating molecule. The long-range Coulomb forces and short-range repulsive forces were both included. The force constants for the host lattice as well as that around the impurity were obtained in terms of Kellermann's A and B constants[5] (see Sec. II), which were evaluated from compressibility data. The charge on each ion was assumed to be $\pm e$. The highest triply degenerate mode was matched with the observed local mode frequency by varying the near-neighbor force constant around the impurity.

The molecular model of a point defect will possess several electric-dipole-active normal mode frequencies. If the defect mass is smaller than the host-lattice ion masses, as is the case for the F and U centers, one of the eigenfrequencies should be identified as the local mode and another as the gap mode. The other eigenfrequencies of the system, that are either dipole active or Raman active, may be identified with defect-activated resonant-band modes.[6] Following the suggestion of Rosenstock and Klick,[2] we believe that the local mode due to the F center is the F band observed in the visible region for most alkali halides. It is the purpose of this paper to predict the position and the intensity of the gap mode from a molecular model of the F center, which incorporates, with certain modifications, the conjecture of Rosenstock and Klick[2] and the molecular model of Jaswal.[4] It is, however, realized that the proposed model is a classical harmonic-oscillator model and obviously is unable to explain the multifarious properties of the F center including that of the F-band shape for which a number of quantum-mechanical models exist.[7] Nevertheless, as far as the infrared-active gap mode associated with the F center is concerned, it will be shown that the present model proves to be adequate.

II. MOLECULAR MODEL

We consider the impurity mass M_0 to be situated at the origin and its six neighbors at $(\pm 1, 0, 0)r$, $(0, \pm 1, 0)r$, and $(0, 0 \pm 1)r$, where r is the near-neighbor distance in an NaCl-type lattice. The seven-particle system has O_h point-group symmetry. Each particle has three degrees of freedom, and the displacement vectors provide a basis for a reducible representation of the group. The total representation Γ decomposes into the following irreducible representations:

$$\Gamma = A_{1g} + E_g + F_{1g} + F_{2g} + 3F_{1u}(F'_{1u}, F''_{1u}, F'''_{1u}) + F_{2u} \ .$$

Here F_{1g}, F_{2g}, and F_{2u} are shear modes. The normal modes which will contribute to the Raman spectra are A_{1g}, E_g, and F_{2g} types, and are expected to be relatively independent of the defect mass as it remains stationary for these modes

of oscillation. The F_{1g} and F_{2u} shear modes are neither Raman nor infrared active, and the three F_{1u}-type modes are infrared active.[8] Of these the displacement of the defect mass M_0 is largest in F'_{1u} only. In the case of F''_{1u} and F'''_{1u} modes, M_0 moves either in the same direction as the other two near neighbors lying on the same axis or very little compared to the near neighbors. Therefore, F''_{1u} and F'''_{1u} eigenfrequencies will be relatively insensitive to the defect mass.

The equations of motion for this seven-particle system can be written as

$$M_l \ddot{u}_\alpha(l) = -\sum_{\alpha',l'} \Phi_{\alpha\alpha'}(l,l') u_{\alpha'}(l') \ , \tag{1}$$

which leads to

$$\omega^2 W_\alpha(l) = \sum_{l',\alpha'} D_{\alpha\alpha'}(l,l') W_{\alpha'}(l) \ , \tag{2}$$

where $\alpha, \alpha' = x, y, z$; $l, l' = 0$ for the impurity and $l, l' = 1, 2, \ldots, 6$ for the near neighbors; and

$$D_{\alpha\alpha'}(l,l') \equiv (M_l M_{l'})^{-1/2} \left. \frac{\partial^2 \Phi}{\partial u_\alpha(l) \partial u_{\alpha'}(l')} \right|_0$$

evaluated at the equilibrium position. M_l represents the mass of the lth ion. $u_\alpha(l)$, the αth component of the displacement of the lth ion, is given by

$$u_\alpha(l) = (M_l)^{-1/2} W_\alpha(l) e^{i\omega t} \ .$$

We assume that except for this particle system the rest of the lattice is stationary. We also assume that the ions are polarizable and have an effective charge $e^*(<e)$. It is further assumed that the impurity ion has the same effective charge. For the F-center impurity the latter assumption may be justified in the following manner: (i) The crystal with the impurity is electrically neutral, and (ii) ENDOR experiments show[9] that the F-center electron spreads out sometimes up to the fourth or fifth nearest neighbor.

The potential energy Φ consists of Coulomb and short-range repulsive parts,

$$\Phi = \sum_{i,j} [e^*(i)e^*(j)/|r_{ij}| + V(|r_{ij}|)], \tag{3}$$

where the summation is over all possible ion pairs. We introduce two sets of Kellermann constants,[5] A_1, B_1 for the host lattice, and A_2, B_2 for the impurity site. A_1 and B_1 are defined as

$$V' \equiv \left(\frac{\partial V}{\partial r}\right)_0 = \frac{1}{2}\left(\frac{e^2}{V_a}\right) r_0 B_1 \ ,$$
$$V'' \equiv \left(\frac{\partial^2 V}{\partial r^2}\right)_0 = \frac{1}{2}\left(\frac{e^2}{V_a}\right) A_1 \ , \tag{4}$$

where r_0 is the equilibrium nearest-neighbor separation of the host-lattice crystal and $V_a = 2r_0^3$. It is further assumed that there is no relaxation around the impurity. This leads to $B_1 = B_2 = B$. This also means that the unit-cell volume V_a is the same for the impurity site as it is for the rest of the host lattice. Wood and Joy[10] have shown that a change in volume occurs in the form of near neighbors moving radially inwards when F centers are introduced in an alkali halide. However, the volume change is less than 5% and shall not affect our calculations drastically.

The equilibrium condition $d\Phi/dr\big|_0 = 0$ yields $B = -\frac{2}{3}Z^2\alpha_M$, where α_M is the Madelung constant equal to 1.74756 for the NaCl structure and $Z = e^*/e$. The constants A_1 and e^* are evaluated by fitting $\vec{k} \sim 0$ LO- and TO-phonon frequencies[11] as follows:

$$\mu V_a \omega_{\rm LO}^2 / e^2 = f_1 + \tfrac{8}{3}\pi Z^2 \ , \tag{5}$$

and

$$\mu V_a \omega_{\rm TO}^2 / e^2 = f_1 - \tfrac{4}{3}\pi Z^2 \ , \tag{6}$$

where $f_1 \equiv A_1 + 2B - (32\pi^2\alpha/9V_a) Z^2$.

The term μ is the reduced mass and the polarizability α is given by the Clausius-Mossotti formula

$$\alpha = (3V_a/4\pi)[(\epsilon_\infty - 1)/(\epsilon_\infty + 2)] \ , \tag{7}$$

where ϵ_∞ is the high-frequency dielectric constant. With the experimental values of $\omega_{\rm LO}$, $\omega_{\rm TO}$, and ϵ_∞, the constants A_1 and e^*/e are evaluated for NaBr, NaI, KBr, and KI, crystals that are known to have gaps between acoustic and optic bands. These are given in Table I. For the defect site

$$f_2 \equiv A_2 + 2B - 32\pi^2\alpha Z^2/9V_a \ , \tag{8}$$

where A_2 is treated as a variable.

III. RESULTS AND DISCUSSION

The secular equation (2) is solved for eigenvalues and eigenvectors as functions of A_2 and M_0. The method for computing $D_{\alpha\alpha'}(ll')$ has been given by Jaswal[4] and is not further elaborated upon. In each case the highest frequency was found to be triply degenerate with eigenvectors of the F_{1u} type. To find the desired A_2, the experimentally observed F-center absorption peak was matched with the highest F_{1u} eigenfrequency (F'_{1u}). We have used the F-band absorption peak frequency rather than the emission peak frequency to determine A_2. This may be justified because the F center has a rather long lifetime[12] and the local symmetry is lowered in the emission process. Similarly, for the H^- center, the matching frequency was the local mode frequency. The experimental values used, the constant A_2, and the force-constant softening are given in Table I. The following observations may be made: (i) $A_1 > A_2$ or $f_2/f_1 < 1$, and (ii) $(f_2)_{F\ \rm center} < (f_2)_{H^-\rm center}$

TABLE I. Experimental data used and the force constant softening.

Crystal	e^*/e	A_1 [a]	Local mode peak (cm^{-1})		A_2		(f_2/f_1) (in units of 10^{-2})		Temp
			F band [b]	H^- center	F center	H^- center	F center	H^- center	(°K)
KI	0.68	13.87 [c]	15 006	382 [d]	8.13	9.20	50.3	59.5	4
KBr	0.76	13.06	15 889	440 [e]	6.71	8.41	40.8	56.6	300
NaI	0.68	10.73	17 020	431 [f]	8.27	9.40	70.8	84.2	300
NaBr	0.72	10.83	18 551	493 [e]	7.30	8.71	58.5	75.1	300

[a] ω_{LO} and ω_{TO} data are from S. Nudelman and S. S. Mitra, *Optical Properties of Solids* (Plenum, New York, 1968), p. 413.

[b] From Ref. 7, p. 11.

[c] From G. Benedek and A. A. Maradudin, J. Phys. Chem. Solids 29, 423 (1968).

[d] From B. Fritz, U. Gross, and D. Bäuerle, Phys. Status Solidi 11, 231 (1965).

[e] From G. Schäfer, J. Phys. Chem. Solids 12, 233 (1960).

[f] From A. A. Maradudin, Solid State Phys. 19, 14 (1966).

However, the most interesting point to note is that the force-constant softening due to the F center is approximately the same as that for the U center, confirming Rosenstock and Klick's original contention[2] that the F absorption band is in reality the local mode due to the F-center electron.

As expected, the frequencies of the symmetric modes (g type) were found to be independent of the impurity mass. F''_{1u}- and F'''_{1u}-type modes were also found to be nearly mass independent. The F'_{1u} mode, on the other hand, was very sensitive to the defect mass. To illustrate this, the eigenfrequencies and the eigenvectors of matrix $[D_{\alpha\alpha'}(l,l')]$ were computed for KI as a function of M_0 with $A_1 = 13.87$, $A_2 = 9.2$, and $e^*/e = 0.681$. The eigenfrequencies of F'_{1u} were found to be 16 316 cm^{-1} for the electron mass and 382 cm^{-1} for the hydrogen mass; those of F''_{1u}, 82.40 cm^{-1} for the electron, and 82.38 for the hydrogen mass. Clearly, the F''_{1u} frequency is independent of M_0. However, one expects a small change in the force constant as one replaces one kind of center by another nonisotopic center (see Table I). Thus, any slight change in the eigenfrequency for this mode will arise mainly from a change in the force constant. Results for the F center in KI, NaBr, and NaI are given in Table II. Similar results were also obtained for the U center. Comparing these eigenfrequencies for each normal mode it was found that except for the highest eigenfrequency (F'_{1u}) all other frequencies associated with the H^- ion were only 1–3 cm^{-1} higher than the corresponding eigenfrequencies associated with the F center.

The F''_{1u} and F'''_{1u} modes are infrared active and the former is situated in the gap between the optic and acoustic bands of the host lattice. For the F center in KI a sharp band at 83 cm^{-1} and a rather broad band peaking around 63 cm^{-1} have been observed[1] in the far-infrared absorption. Clearly, these should be compared with the calculated frequencies of 81.2 cm^{-1}(F''_{1u}) and 65.5 cm^{-1} (F'''_{1u}). More recently, Baüerle[13] has reported the observation of a gap mode in KI:H^- also at about 82 cm^{-1}, although somewhat weaker than the F-center gap-mode absorption. This compares very well with our value of 82.4 cm^{-1} for this center. A resonant-band mode peaking around 62 cm^{-1} has also been reported[6,14] for this system. Our calculated value of 66 cm^{-1} is not too far from this. There have been no far-infrared measurements to date for F centers in KBr, NaBr, and NaI. The far-infrared absorption spectrum[14] of KBr:H^- at 7 °K shows structures below 93 cm^{-1}, while our calculation based on parameters evaluated at 300 °K shows two eigenfrequencies at 94 cm^{-1} (F''_{1u}) and 76 cm^{-1} (F'''_{1u}). To our knowledge no far-infrared measurements have so far been done on NaBr:H^- and NaI:H^-.

Since the present calculations also yield the

TABLE II. Calculated eigenfrequencies for the molecular model of the F center.

Crystal	Eigenfrequencies (cm^{-1})							
	$\Gamma_1(A_{1g})$	$\Gamma_{12}(Eg)$	$\Gamma'_{15}(F_{1g})$	$\Gamma'_{25}(F_{2g})$	$\Gamma_{15}(F'_{1u})$	$\Gamma_{15}(F''_{1u})$	$\Gamma_{15}(F'''_{1u})$	$\Gamma_{25}(F_{2u})$
KI	51.8	78.4	88.6	70.7	15006	81.2	65.5	75.2
KBr	55.5	90.7	101.0	82.2	15889	92.6	74.3	88.0
NaI	63.1	106.7	109.3	83.7	17020	103.4	84.9	91.7
NaBr	70.3	124.4	130.9	100.6	18551	120.2	99.4	110.1

eigenvectors, the ratio of the integrated intensities of the F'_{1u} to F''_{1u} modes may be calculated. For the F center in KI the calculated value of this ratio is about 9×10^6. An approximate estimate of the experimental intensity ratio of the F-band to the F-center gap mode in the same crystal can be made using the data of Baüerle and Fritz[1] and the oscillator strength of the F band.[15] This yields a value of 10^6 within an order of magnitude of the calculated value.

The second type of experiment which shows impurity-induced gap-mode and band-mode phonons is Raman scattering.[16,17] The only system studied in detail[17] is the F center in NaBr. A number of features of the observed spectrum agree with our calculated values, although not in entirety. In any case, a simple model as presented here is not expected to predict the most of the critical-point phonon frequencies of the host lattice that may become optically active as a result of the relaxation of the $\vec{k}$ selection rule in the presence of an impurity and may show up as features in the Raman spectrum. Nevertheless, detailed measurements of Raman spectra of F centers in KI, KBr, and NaI and that of the U centers in any of the alkali halides will be of great interest.

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