PHYSICAL REVIEW VOLUME 154, NUMBER 3 15 FEBRUARY 1967

Raman Scattering by Color Centers*

G. Benedek and G. F. Nardelli†
Istituto di Fisica dell'Università, Milan, Italy

(Received 15 August 1966)

It is pointed out that the Raman spectrum of a color center gives significant information on the vibration spectrum associated with an electronic transition of the center itself. The formal theory of the first-order Raman scattering by substitutional defects in alkali halides is developed in detail. The coupling coefficients according to which the irreducible representations of the perturbed normal modes enter the total Raman spectrum are shown to be simply related to the stress coefficients of the absorption band. Calculations on the first-order Raman spectra of F centers in NaCl and KCl are found to be in fairly good agreement with experimental data recently obtained. An application of the present method to the theory of local-mode sidebands is also outlined.

I. INTRODUCTION

The energy levels of an electron bound at a defect in a crystal lattice are usually quite dependent on the position of the neighbor atoms. Thus the electronic transitions induced by an external radiation field can be accompanied by excitation or absorption of phonons of the lattice. As we are concerned with an imperfect lattice, perturbed phonons are involved. The perturbed phonons can be suitably classified according to the irreducible representations of the point group pertaining to the local perturbation due to the defect. The irreducible representations according to which the lattice is allowed to vibrate depend on the particular kind of the perturbation. The phonon irreducible representations which couple with an electron transition (say a dipole transition) are selected on simple symmetry considerations, i.e., by means of group theory; but the theoretical evaluation of the coupling coefficient for each allowed irreducible representation, describing the intensity and details of the vibronic spectra, requires knowledge of the electron wave functions for each given lattice configuration, in the framework of the Born-Oppenheimer approximation. As at present this kind of problem appears to be very hard, the phenomenological approach seems to be more advantageous for investigating the coupling between the bound electrons and the lattice vibrations. From this point of view the study of the effects that an applied stress has on the optical absorption of color centers[1,2] seems likely to give significant information on such coupling coefficients, because the internal strains produced by an elastic deformation and the local vibrating strains supported by the perturbed phonons assisting an electronic dipole transition usually have the same symmetries.

One of the most direct methods of investigating the phonon spectrum associated with an electronic transition seems to be the study of the Raman spectrum of an imperfect lattice, particularly when the perfect host lattice does not allow first-order Raman scattering (as in alkali halides). Indeed, when the frequency ω_0 of the incident light is far enough from an electron dipole transition frequency ω_T, all that the electron can do is to polarize itself and to induce a dipole moment $\mathbf{M}$ which radiates scattered light of frequency ω. Since the electron polarization consists in a mixing of the ground state with the optic-active excited states, the vibrational modes and the coupling coefficients involved in this process are the same as those assisting the absorption process. In this paper we outline briefly the theory of Raman scattering in crystals, with particular reference to the phenomenology of first-order processes induced by defects in alkali halides. This restriction would not in principle forbid us to investigate the case of strong electron-phonon coupling, since we are dealing with a virtual electron transition. Indeed the comparison between the theoretical and experimental[3] Raman spectra of the F-center turns out to be satisfactory, so that the quantitative investigation of the electron-phonon interaction near imperfections through the analysis of first-order Raman spectra seems to be feasible.

II. FORMAL THEORY

The relation between the intensities of the incident and scattered electromagnetic fields is fully exhibited by the fourth-order frequency-dependent tensor.[4,5]

$$i_{\alpha\gamma\beta\lambda}(\Omega)=(2\pi)^{-1}\int_{-\infty}^{+\infty} dt\, e^{-i\Omega t}\langle P_{\beta\lambda}(t)P_{\alpha\gamma}{}^{*}(0)\rangle\,, \quad (1)$$

where $\Omega=\omega_0-\omega$, $P_{\beta\lambda}(t)$ is the time-dependent operator for the electronic polarizability tensor of the crystal, and $\langle\cdots\rangle$ denotes a thermal average at the absolute temperature T.

The fact that we are concerned with a fourth-order tensor is clarified by the analogy between the classical Raman response and the theory of elasticity. The Max-

---

* This research has been sponsored by EOAR under Grant No. 65-05 with the European Office of Aerospace Research, U. S. Air Force. A preliminary account of this work has been presented at the Conference on Localized Excitations in Solids, Milan, 1966.

† Italian National Council for Research, Gruppo Nazionale di Struttura della Materia.

[1] W. Gebhardt and K. Meier, Phys. Status Solidi 8, 303 (1965).

[2] S. E. Schnatterly, Phys. Rev. 140, A1364 (1965).

[3] J. M. Worlock and S. P. S. Porto, Phys. Rev. Letters 15, 697 (1965).

[4] A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 19.

[5] N. X. Xinh, thesis, Faculté des Sciences de l'Université de Paris, 1966 (unpublished).

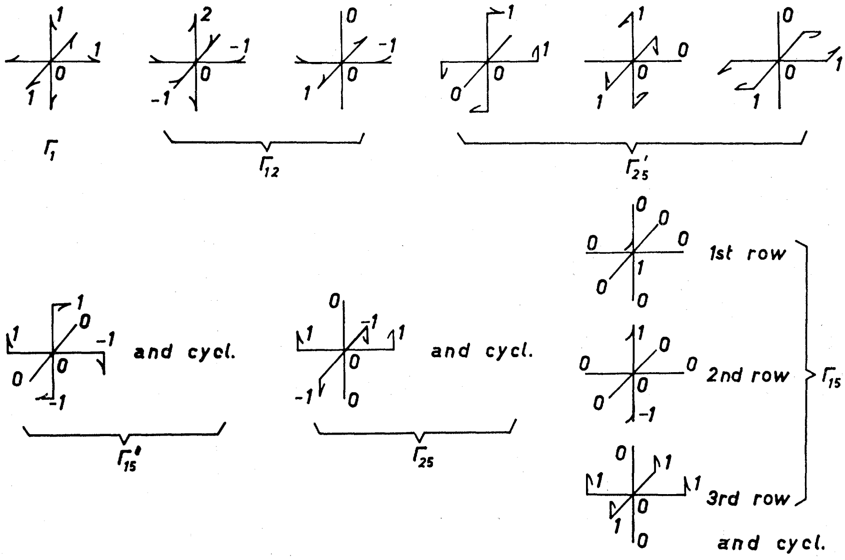

FIG. 1. Symmetry coordinates for a local change in mass and in central and noncentral nearest-neighbor force constants in a NaCl-type lattice.

well tensors of the incident and diffused light can be put in correspondence with the stress and strain tensors, respectively; then $i_{\alpha\gamma\beta\lambda}(\Omega)$ plays the same role as the elastic tensor. However, the polarizability $P_{\beta\lambda}(t)$, which is in general a complex function of the incident-light frequency ω_0, as well as of the nuclear displacements $\mathbf{u}(\mathbf{l},\kappa)$ ($\mathbf{l}$ being a Bravais vector and κ a cell index), can be split into Hermitian and anti-Hermitian parts; the anti-Hermitian part derives from the existence of the transition frequency ω_T, which introduces absorption damping. When ω_0 is not too close to ω_T, the tensor $P_{\beta\lambda}$ can be considered to a good approximation to be a real, i.e., symmetric, tensor; and so can $i_{\alpha\gamma\beta\lambda}(\Omega)$ with respect to the first and second couples of indices, just like the elastic tensor. The symmetry of the scattering center by itself defines the number of nonzero independent components of $i_{\alpha\gamma\beta\delta}(\Omega)$. For cubic symmetry we have only three independent components, namely, $i_{xxxx}=i_{11}$, $i_{xxyy}=i_{12}$, and $i_{xyxy}=i_{44}$.

With regard to the dependence on the nuclear displacements, we can expand the polarizability $P_{\alpha\gamma}$ in powers of $\mathbf{u}(\mathbf{l},\kappa)$: the zero-order term [independent of $\mathbf{u}(\mathbf{l},\kappa)$, i.e., no phonons involved] accounts for the Rayleigh scattering ($\Omega=0$), while the first- and higher order terms account for the first- and higher order Raman scattering, respectively. The first-order process is characterized by the coefficient

$$P_{\alpha\beta/\mu}(\mathbf{l},\kappa)\equiv\partial P_{\alpha\beta}/\partial u_\mu(\mathbf{l},\kappa)\,. \qquad (2)$$

At a given lattice site $(\mathbf{l},\kappa)$, the polarizability $P_{\alpha\beta/\mu}(\mathbf{l},\kappa)$ transforms like a third-order tensor; its nonzero independent components depend on the point group at $(\mathbf{l},\kappa)$.[6,7] At a point with inversion symmetry all components vanish: indeed no first-order Raman scattering occurs in pure alkali halides. For the neighbor atoms of a substitutional defect in a NaCl-type lattice, $P_{\alpha\beta/\mu}(\mathbf{l},\kappa)$ has a number $N(\mathbf{l},\kappa)$ of independent components as shown in Table I.

TABLE I. Nonzero displacement derivatives of the polarizability tensor.

$\{\mathbf{l},\kappa\}$	Group	$N(\mathbf{l},\kappa)$	Nonzero components $P_{\alpha\beta/\mu}$.
defect(000)	O_h	0	...
1st nearest(100)	C_{4v}	3	$P_{xx/x}$; $P_{yy/x}=P_{zz/x}$; $P_{xy/y}=P_{xz/z}$.
2nd nearest(011)	C_{2v}	5	$P_{xx/x}$; $P_{yy/x}$; $P_{zz/x}$; $P_{xy/y}$; $P_{xz/z}$.
3rd nearest(111)	C_{3v}	4	$P_{11/1}=-2P_{11/2}=-P_{21/2}$; $P_{33/3}$; $P_{31/1}=P_{32/2}$; $P_{11/3}=P_{22/3}$.[a]
...	...	...	...

[a] The indices 1, 2, 3 refer to the orthogonal Cartesian axes (1,1,1), (1, −1, 0), (−1, −1, 2).

We make now the assumption that the electron wave function in the excited states extends not too far from the defect; thus the contributions coming from second and higher orders of neighbors are neglected, and only three parameters enter the first-order part of $i_{\alpha\gamma\beta\lambda}(\Omega)$, Eq. (1). As shown in Ref. 4, when a concentration p of defects is present, the first-order part can be written out explicitly as

$$i_{\alpha\gamma\beta\lambda}{}^{(1)}(\Omega)=(p\hbar\mathfrak{N}(\Omega)/\pi M_{\mp})\sum_{\substack{\mathbf{l}\kappa\mu\\ \mathbf{l}'\kappa'\nu}} P_{\beta\lambda/\nu}(\mathbf{l}\kappa)P_{\alpha\gamma/\mu}(\mathbf{l}'\kappa')$$

$$+\operatorname{Im}(\mathbf{l}\kappa\nu|[I+(L_0-z)^{-1}\Lambda(\Omega)]^{-1}(L_0-z)^{-1}|\mathbf{l}'\kappa'\mu)\,. \qquad (3)$$

Here $z=\Omega^2+2i\Omega 0^+$, L_0 is the dynamical matrix of the host lattice, $\Lambda(\Omega)$ is the frequency-dependent perturbation due to the change of mass and of both central and non-central force constants,[8] Im denotes imaginary part,

---

[6] R. Fieschi and F. G. Fumi, Nuovo Cimento **10**, 865 (1953).

[7] J. F. Nye, in *Physical Properties of Crystals* (Clarendon Press, Oxford, England, 1957), p. 110.

[8] G. Benedek and G. F. Nardelli, in Proceedings of the Conference on Calculations of the Properties of Vacancies and Interstitials, Skiland, Virginia, 1966 (to be published).

and $\mathfrak{N}(\Omega)$ represents the following expressions:

$$\begin{aligned}&[1-\exp(-\hbar\Omega/k_BT)]^{-1}, \quad \Omega>0 \text{ (Stokes process)},\\ &[\exp(\hbar\Omega/k_BT)-1]^{-1}, \quad \Omega<0 \text{ (anti-Stokes process)},\end{aligned} \tag{4}$$

where k_B is the Boltzmann constant. $M_{\mp}$ is the mass of the nearest neighbor. In our case it is convenient to work in the representation of the normalized symmetry coordinates $(\Gamma j|\mathbf{l}\kappa\mu)$ which pertain to the perturbation $\Lambda(\Omega)$. Here Γ is each one of the irreducible representations contained in $\Lambda(\Omega)$, and j refers to the jth partner function of Γ. Equation (3) can be written as

$$i_{\alpha\gamma\beta\lambda}{}^{(1)}(\Omega)=(p\hbar\mathfrak{N}(\Omega)/2\pi M_{\mp}\Omega)\sum_{\Gamma j} P_{\beta\lambda/\Gamma j}P_{\alpha\gamma/\Gamma j}\rho_\Gamma(\Omega)\,, \tag{5}$$

where

$$P_{\alpha\gamma/\Gamma j}=\sum_{\mathbf{l}\kappa\mu} P_{\alpha\gamma/\mu}(\mathbf{l}\kappa)(\Gamma j|\mathbf{l}\kappa\mu) \tag{6}$$

represents the change in polarizability induced by a strain of (Γ,j) type and $\rho_\Gamma(\Omega)$ is the frequency density for the perturbed Γ type of phonons.[8,9] For a perturbation $\Lambda(\Omega)$ extending only to the first neighbors of the defect, the Γ_{15}, Γ_1, Γ_{12}, Γ_{25}', Γ_{15}', and Γ_{25} symmetry modes are allowed to occur in a NaCl-type lattice.[8]

The Γ_{15} modes, the ones which involve the defect mass, are symmetrical with respect to the defect; then $P_{\alpha\gamma/\Gamma_{15}j}\equiv 0$. All the other modes keep the impurity at rest and are antisymmetrical with respect to the defect. Γ_1 and Γ_{12} modes are induced by the local change in the central-force constant λ, while Γ_{25}', Γ_{15}', and Γ_{25} modes are induced by the local change in the noncentral-force constant λ'. Figure 1 shows these symmetry coordinates (or correspondent strains). If $P_{\alpha\gamma}$ is isotropic, only Γ_1 contributes a nonzero strain derivative, as given by Eq. (6); if $P_{\alpha\gamma}$ is symmetrical, Γ_{12} and Γ_{25}' also contribute. As said before, for ω_0 near ω_τ, the tensor $P_{\alpha\gamma}$ can have an antisymmetrical part which transforms according to Γ_{15}'. The symmetry Γ_{25} is never involved.

For the modes we are concerned with, the densities of the one-phonon states read

$$\rho_{\Gamma_1}(\Omega)=(4\Omega M_{\mp}/\lambda)\,\mathrm{Im}\left\{1+\frac{\lambda}{2M_{\mp}}(\mathcal{G}_4{}^{\pm}(\Omega)+2\mathcal{G}_5{}^{\pm}(\Omega))\right\}^{-1}, \tag{7a}$$

$$\rho_{\Gamma_{12}}(\Omega)=(4\Omega M_{\mp}/\lambda)\,\mathrm{Im}\left\{1+\frac{\lambda}{2M_{\mp}}(\mathcal{G}_4{}^{\pm}(\Omega)-\mathcal{G}_5{}^{\pm}(\Omega))\right\}^{-1}, \tag{7b}$$

$$\rho_{\Gamma_{25}'}(\Omega)=(4\Omega M_{\mp}/\lambda')\,\mathrm{Im}\left\{1+\frac{\lambda'}{2M_{\mp}}(\mathcal{G}_6{}^{\pm}(\Omega)+2\mathcal{G}_5{}^{\pm}(\Omega))\right\}^{-1}, \tag{7c}$$

$$\rho_{\Gamma_{15}'}(\Omega)=(4\Omega M_{\mp}/\lambda')\,\mathrm{Im}\left\{1+\frac{\lambda'}{2M_{\mp}}(\mathcal{G}_6{}^{\pm}(\Omega)-2\mathcal{G}_5{}^{\pm}(\Omega))\right\}^{-1}, \tag{7d}$$

where $\mathcal{G}_\mu{}^{\pm}(\Omega)$ are the following complex-valued integrals on the Brillouin zone:

$$\mathcal{G}_4{}^{\pm}(\Omega)=2v_c\sum_s\int d\mathbf{q}\; e_x{}^2(\mp|\mathbf{q}s)\,\sin^2 2\pi aq_x/(\omega_{\mathbf{q}s}{}^2-z)\,, \tag{8a}$$

$$\mathcal{G}_5{}^{\pm}(\Omega)=2v_c\sum_s\int d\mathbf{q}\; e_x(\mp|\mathbf{q}s)e_y(\mp|\mathbf{q}s)\,\sin 2\pi aq_x\,\sin 2\pi aq_y/(\omega_{\mathbf{q}s}{}^2-z)\,, \tag{8b}$$

$$\mathcal{G}_6{}^{\pm}(\Omega)=2v_c\sum_s\int d\mathbf{q}\; e_x{}^2(\mp|\mathbf{q}s)\,\sin^2 2\pi aq_y/(\omega_{\mathbf{q}s}{}^2-z)\,. \tag{8c}$$

$\omega_{\mathbf{q}s}$ and $\mathbf{e}(\mp|\mathbf{q}s)$ denote eigenfrequency and polarization vectors of the host-lattice mode with wave vector $\mathbf{q}$ and branch index s; $2a$ is the lattice constant, and $v_c=2a^3$ the cell volume. It is now interesting to follow an alternative way of reducing the tensor $P_{\alpha\gamma/\mu}(\pm x)$ (where $\pm x$ refers to the two nearest neighbors which are in the x direction). The strain tensor at the defect site for a given antisymmetrical displacement of the neighbors is

$$e_{xy}=u_y(+x)/a\,; \tag{9}$$

since the defect nearest neighbors lie just on the (positive or negative) coordinate axes, $P_{\alpha\beta/\mu}(\pm x)$ can be replaced by the fourth-order tensor

$$P_{\alpha\beta/\mu\nu}\equiv a^{-1}\partial P_{\alpha\beta}/\partial e_{\mu\nu} \tag{10}$$

which is symmetric in $\alpha\beta$ (for $|\omega_0-\omega_\tau|\gg 0$) and $\mu\nu$, and is to be ascribed to the defect site, which has full cubic symmetry. Thus the three independent nonzero components (see also Table I) are

$$P_{xx/xx}\equiv\mathcal{P}_{11}\,,\quad P_{xx/yy}\equiv\mathcal{P}_{12}\,,\quad P_{xy/xy}\equiv\mathcal{P}_{44}\,. \tag{11}$$

---

[9] T. Timusk and M. V. Klein, Phys. Rev. **141**, 662 (1966).

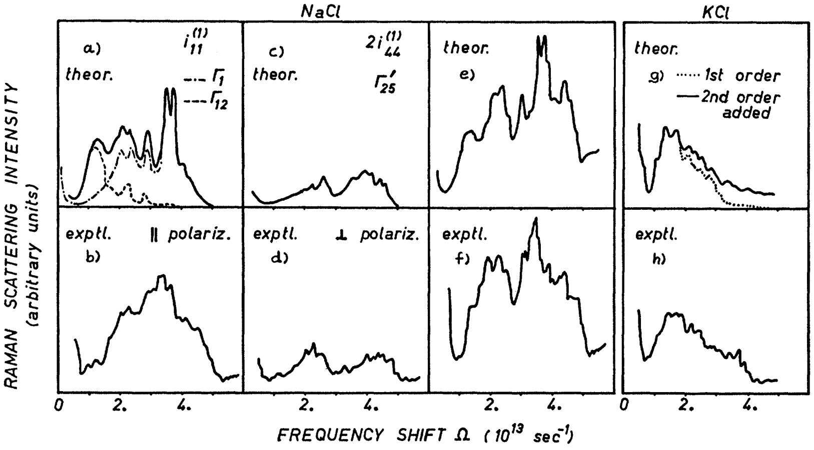

FIG. 2. Theoretical and experimental F-center-induced Raman spectra (Stokes side). NaCl: theoretical first-order (a) and experimental (b) parallel-polarized spectra; theoretical first-order (c) and experimental (d) perpendicular-polarized spectra; theoretical (second-order added) (e) and experimental (f) unpolarized spectra. KCl: theoretical (g) and experimental (h) unpolarized spectra.

In the symmetry coordinate representation, the strains are given by the unitary transformation

$$\begin{aligned} e_{\Gamma_1}&=(e_{xx}+e_{yy}+e_{zz})/\sqrt{3}\,, & e_{\Gamma_{25}',1}&=e_{xy}\\ e_{\Gamma_{12},1}&=(2e_{xx}-e_{yy}-e_{zz})/6^{1/2}, & e_{\Gamma_{25}',2}&=e_{yz}\\ e_{\Gamma_{12},2}&=(e_{zz}-e_{yy})/\sqrt{2}\,, & e_{\Gamma_{25}',3}&=e_{zx}\end{aligned} \tag{12}$$

and the nonzero symmetry strain derivatives are

$$\begin{aligned} P_{xx/\Gamma_1}&=P_{yy/\Gamma_1}=P_{zz/\Gamma_1}=\sqrt{3}^{-1}(\mathcal{P}_{11}+2\mathcal{P}_{12})\\ P_{xx/\Gamma_{12},1}&=-2P_{yy/\Gamma_{12},1}=-2P_{zz/\Gamma_{12},1}\\ &=(2/6^{1/2})(\mathcal{P}_{11}-\mathcal{P}_{12}) \qquad (13)\\ P_{xy/\Gamma_{25}',1}&=P_{yz/\Gamma_{25}',2}=P_{zx/\Gamma_{25}',3}=\mathcal{P}_{44}\,.\end{aligned}$$

The components of the first-order Raman tensor for cubic crystals read finally

$$\begin{aligned} i_{11}{}^{(1)}&=(p\hbar\mathcal{N}(\Omega)/6\pi M\mp\Omega)\{(\mathcal{P}_{11}+2\mathcal{P}_{12})^2\rho_{\Gamma_1}(\Omega)\\ &\qquad+2(\mathcal{P}_{11}-\mathcal{P}_{12})^2\rho_{\Gamma_{12}}(\Omega)\}\,,\\ i_{12}{}^{(1)}&=(p\hbar\mathcal{N}(\Omega)/6\pi M\mp\Omega)\{(\mathcal{P}_{11}+2\mathcal{P}_{12})^2\rho_{\Gamma_1}(\Omega)\\ &\qquad-(\mathcal{P}_{11}-\mathcal{P}_{12})^2\rho_{\Gamma_{12}}(\Omega)\}\,, \qquad (14)\\ i_{44}{}^{(1)}&=(p\hbar\mathcal{N}(\Omega)/6\pi M\mp\Omega)\{3\mathcal{P}_{44}{}^2\rho_{\Gamma_{25}'}(\Omega)\}\,,\end{aligned}$$

where $i_{11}{}^{(1)}$, $i_{12}{}^{(1)}$, and $i_{44}{}^{(1)}$ have been defined already.

III. THE COUPLING COEFFICIENTS

At this point the formal theory is fully developed: every quantity in Eqs. (14) can be numerically evaluated, except for the coefficients $\mathcal{P}_{ij}$. We try now to express these coefficients in terms of quantities which can be measured experimentally, namely, the oscillator strength f, and the hydrostatic, axial, and trigonal coefficients A, B, and C, respectively,[1,2] which describe the shift and splitting of the absorption peak under external stresses. Assume for our electron only one threefold degenerate excited state of configuration $2p$ (Γ_{15} in cubic crystals), while the ground state is $1s$ (Γ_1). For a suitable set of displacements $\{\mathbf{u}(l\kappa)\}$, here denoted for brevity by X, the degeneracy of the $2p$ state is fully resolved and there are three transition frequencies $\omega_{\tau,i}$ ($i=1,2,3$) which depend on X. Notice that X is just the usual configurational coordinate. For $|\omega_0-\omega_{\tau,i}|\gg\Omega$, the polarizability tensor can be written as[10]

$$P_{\alpha\beta}(X)=\frac{1}{3\hbar}\sum_{i=1}^{3}\frac{2\omega_{\tau,i}}{\omega_{\tau,i}{}^2-\omega_0{}^2}M_{\tau,\alpha}{}^{*(i)}(X)M_{\tau,\beta}{}^{(i)}(X)\,. \tag{15}$$

The index $i=1$, 2, 3 labels the principal axes of the strain dyadic, and

$$M_{\tau,\alpha}{}^{(i)}(X)\equiv e(2p,i|x_\alpha|1s) \tag{16}$$

is the dipole moment of the transition, e and $\mathbf{x}$ being the charge and the position vector of the electron. For the equilibrium configuration $X=X_{1s}$ of the ground state,

$$|\mathbf{M}_\tau(X_{1s})|^2=3f\hbar e^2/2m\omega_\tau; \tag{17}$$

m is the electron mass; here the superscript (i) is irrelevant. In a first-order approximation, i.e., when we keep the electronic functions unchanged, it is found that

$$\begin{aligned} P_{xx/\Gamma_1}&=\sqrt{3}AK(\omega_0)\,,\\ P_{xx/\Gamma_{12},1}&=-2P_{yy/\Gamma_{12},1}=(2\sqrt{6})BK(\omega_0)\,, \qquad (18)\\ P_{xy/\Gamma_{2s}',1}&=CK(\omega_0)\,,\end{aligned}$$

while, in agreement with the symmetry predictions, all the other noncyclic derivatives are found to be zero. We have put

$$K(\omega)=(fe^2/am)[2\omega_\tau/(\omega_\tau{}^2-\omega^2)^2]\,. \tag{19}$$

Thus,

$$\begin{aligned} \mathcal{P}_{11}&=K(\omega_0)\{A+4B\}\,,\\ \mathcal{P}_{12}&=K(\omega_0)\{A-2B\}\,, \qquad (20)\\ \mathcal{P}_{44}&=K(\omega_0)C\,,\end{aligned}$$

and

$$\begin{aligned} i_{11}{}^{(1)}&=(p\hbar\mathcal{N}(\Omega)/6\pi M\mp\Omega)K^2(\omega_0)\\ &\qquad\times\{9A^2\rho_{\Gamma_1}(\Omega)+72B^2\rho_{\Gamma_{12}}(\Omega)\}\,,\\ i_{12}{}^{(1)}&=(p\hbar\mathcal{N}(\Omega)/6\pi M\mp\Omega)K^2(\omega_0)\\ &\qquad\times\{9A^2\rho_{\Gamma_1}(\Omega)-36B^2\rho_{\Gamma_{12}}(\Omega)\}\,, \qquad (21)\\ i_{44}{}^{(1)}&=(p\hbar\mathcal{N}(\Omega)/6\pi M\mp\Omega)K^2(\omega_0)\{3C^2\rho_{\Gamma_{25}'}(\Omega)\}\,.\end{aligned}$$

---

[10] D. A. Kleinman, Phys. Rev. **134**, A423 (1964).

TABLE II. Values of the parameters used in the calculation of the F-center Raman spectra and vibrational resonant frequencies.

Crystal	Stress coefficients (eV) $-A$	$-B$	$-C$	Change in nn force constant λ/f_{eff}	Resonance frequencies (10^{13} sec^{-1}) Γ_1	Γ_{12}
NaCl(F center)	1.52	0.28	1.14	-0.8	···	1.50 2.40 2.31
KCl(F center)	1.26	0.54	1.30	-0.6	···	···

A, B, and C are the hydrostatic, axial, and trigonal coefficients, respectively.

IV. NUMERICAL RESULTS AND CONCLUSIONS

As we have a reliable experimental knowledge of the coefficients A, B, C,[1,2] and of the Raman spectra[3] for F-center-doped NaCl and KCl at $T=77°$K (see Table II), the calculated functions $i_{11}^{(1)}$, $i_{44}^{(1)}$, and $i_{11}^{(1)}+i_{44}^{(1)}$ should allow for a direct comparison with the experimental "parallel-polarized," "perpendicular-polarized," and unpolarized spectra, respectively (Fig. 2), in these crystals.[3] The experimental data here reported do not permit us to make a comparison between intensities. Our information on both experimental and theoretical second-order Raman spectra of the pure host crystal[11–13] allows us to correct the theoretical first-order spectra for the bulk second-order contribution. The densities of states $\rho_\Gamma(\Omega)$ for each representation involved in Eqs. (7) have been calculated by using Hardy's deformation-dipole model[14] for the host lattice dynamics with $T=0°$K input data and a grid of 4096 points in the Brillouin zone; different values of λ were employed, while λ' (which is of order -0.2λ) was taken to be zero (notice that Eqs. (7c) and (7d) retain their meaning).

In the case of the F center in NaCl and KCl crystals, the best fit to the experimental spectra is obtained for $\lambda=-0.8f_{\text{eff}}$ and $\lambda=-0.6f_{\text{eff}}$, respectively, f_{eff} being the nearest-neighbor effective force constant for the host lattice[8]: These values of λ are found to be consistent with the values estimated *a priori* by assuming a Born-Mayer potential for the second-neighbor repulsive interaction between the positive ions around the F center and using reasonable values for the local defect of ionic charge and nearest-neighbor inward relaxation for the F center in the ground state ($\approx -10\%$). The present value of λ for KCl accounts also for the F-center-induced low-frequency resonant mode deduced from thermoconductivity measurements.[15] In Table II the resonance frequencies corresponding to the chosen λ values are reported. For realistic values of λ', no resonance occurs for "noncentral" representations.

It should be noted that, when the resonant mode falls into a region of high density of frequencies, only a broad peak is expected in the shape of $\rho_\Gamma(\Omega)$: this occurs for the F center, as shown in Fig. 2. The agreement between calculated and experimental spectra (Fig. 2) seems to be satisfactory, provided that the second-order Raman spectrum of the host lattice, occurring in the high-frequency region, is added to $i_{ij}^{(1)}$. The discrepancies could be ascribed to the anharmonicity effects on vibrations (particularly the third-order one due to the asymmetrical potential well of the neighbor atoms) are expected to be important at $T=77°$K. The following test of the validity of our calculations is obtained from the Raman data on KCl:I$^-$. After deducing the value of λ ($\lambda=0.3f_{\text{eff}}$) from fitting the Γ_{15}-resonance frequency on that observed in thermoconductivity measurements[16] and by using reasonable values for the coupling coefficients, the Raman spectrum is found to exhibit a strong structure centered at $\omega=1.20\times10^{13}$ sec^{-1}, which agrees with that observed by Stekanov and Eliashberg.[17] We conclude that:

(i) The observed Raman spectra of the F center are to be ascribed to impurity-induced first-order Raman scattering, even if they do not present sharp resonance peaks;

(ii) The accurate analysis of the Raman spectra combined with a good knowledge of the vibrational states is able to give deep insight into the electron-phonon interaction at color centers;

(iii) The method used in Sec. III for determining the coupling coefficients can be easily applied to the case in which odd-parity perturbed normal modes are involved in the excitation of the optic-active Γ_{15} local mode (sidebands of U center in alkali halides). Stress experiments on the infrared U-band would enable us to obtain the coupling coefficients which weight the irreducible representations occurring in the sidebands. Details on this topic are given elsewhere.[18]

---

[11] H. L. Welsh, M. F. Crawford, and W. J. Staple, Nature **164**, 737 (1949).

[12] A. C. Menzies and J. Skinner, J. Phys. Radium **9**, 93 (1948); **9**, 60 (1948).

[13] A. M. Karo and J. H. Hardy, Phys. Rev. **141**, 696 (1966).

[14] J. R. Hardy, Phil. Mag. **7**, 315 (1961).

[15] C. T. Walker, Phys. Rev. **132**, 1963 (1963).

[16] C. T. Walker and R. D. Pohl, Phys. Rev. **131**, 1433 (1963).

[17] A. J. Stekanov and M. B. Eliashberg, Fiz. Tverd. Tela **5**, 2985 (1963) [English transl.: Soviet Phys.—Solid State **5**, 2185 (1964)].

[18] G. Benedek and G. F. Nardelli, Phys. Rev. Letters, **17**, 1137 (1966).