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PHYSICAL REVIEW B VOLUME 2, NUMBER 10 15 NOVEMBER 1970

Ionic Raman Effect. I. Scattering by Localized Vibration Modes

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(Received 22 June 1970)

A theory is presented of the Raman scattering of infrared light by the modulation of the ionic contribution to the polarizability of a crystal by the displacements of the atoms from their equilibrium positions. It is applied to the calculation of the scattering efficiency for the scattering of light by the localized vibration modes due to H^- U centers in CaF_2. The results of these calculations indicate that such scattering should be readily observable when a CO or He-Ne laser is used as the source of incident light.

It is convenient to regard the Raman scattering of light by the elementary excitations of a crystal as the scattering of light by the inhomogeneities in the refractive index, or the polarizability, of the crystal caused by the elementary excitations being probed. In the case of the inelastic scattering of light by the lattice vibrations of a crystal, the polarizability contains two contributions, an ionic contribution and an electronic contribution. In standard treatments of the theory of the Raman effect,[1] the ionic part of the polarizability is neglected in comparison with the electronic part, because the frequency of the incident light is large compared with the transition frequency between the vibrational states of the crystal corresponding to the electronic ground state. However, with the introduction of infrared lasers, such as the CO_2 laser, which emits at 10.6 μ (943 cm^{-1}), we now have sources of light for Raman scattering experiments whose frequencies are comparable with the transition frequencies between vibrational states of a crystal. Consequently, it seems worth while to investigate the contribution to the Raman scattering of light arising from the modulation of the ionic part of the crystal polarizability by the atomic displacements.

In this paper we study this contribution in isolation from the contribution arising from the modulation of the electronic part of the polarizability by the atomic displacements, and from possible interferences between these two scattering mechanisms. Although our purpose in doing so is to focus attention on the ionic Raman effect and to display some of its features, it is also the case that the scattering arising from the modulation of the electronic part of the polarizabilty by the atomic displacements is expected to be very weak for incident light in the infrared range. This is because the scattering efficiency is proportional to the fourth power of the frequency of the scattered light.[1] For incident light in the visible, the difference between the frequencies of the incident and scattered light can be neglected with little error. In going to the infrared, the frequency of the scattered light decreases by a factor of as much as 20, so that the scattered intensity decreases by a factor of 1.6×10^5. If the scattering is weak to begin with, a decrease in its intensity by a factor of this magnitude may render it unobservable. In the ionic Raman effect, on the other hand, there exists the possibility of resonance denominators occurring of such a type that the proportionality of the scattered intensity to the fourth power of the scattered frequency is cancelled. Consequently, the possibility exists that for incident frequencies in the infrared the ionic Raman effect dominates the electronic effect.

The starting point for our discussion is the expression for the intensity per unit solid angle of light scattered into the frequency interval $(\omega_s, \omega_s + d\omega_s)$,[1]

$$I(\omega_s)d\omega_s = \frac{\omega_s^4}{2\pi c^3} \sum_{\alpha\beta\gamma\lambda} n_\alpha n_\beta\, i_{\alpha\gamma\beta\lambda}(\Omega) E_\gamma^- E_\lambda^+ \, d\omega_s \ , \tag{1}$$

where c is the speed of light, $\vec{n}$ is a unit vector which selects the polarization of the scattered light, and $\vec{E}^-$ and $\vec{E}^+$ $(=\vec{E}^{-*})$ are the amplitudes of the negative and positive frequency components of the electric field of the incident light, respectively. The frequency $\Omega = \omega_s - \omega$ is the shift in the frequency of the light on scattering, where ω is the frequency of the incident light. The coefficient $i_{\alpha\gamma\beta\lambda}(\Omega)$ is given by

$$i_{\alpha\gamma\beta\lambda}(\Omega) = \sum_{vv'} p_v P_{\beta\lambda}^{vv'}(\omega)[P_{\alpha\gamma}^{vv'}(\omega)]^* \delta(\Omega - \omega_{vv'}) \ , \tag{2}$$

where v and v' denote initial and final vibrational states of the crystal corresponding to the electronic ground state, p_v is the Boltzmann weighting factor, and $\omega_{vv'} = (\mathcal{E}_v - \mathcal{E}_{v'})/\hbar$, where $\mathcal{E}_v$ and $\mathcal{E}_{v'}$ are the energies corresponding to the eigenstates $|v)$ and $|v')$, respectively. The function $P_{\alpha\beta}^{vv'}(\omega)$ is defined by

$$P_{\alpha\beta}^{vv'}(\omega) = \frac{1}{\hbar} \sum_{v''} \frac{(v|M_\alpha|v'')(v''|M_\beta|v')}{\omega_{v''v'} + \omega - i\gamma} + \frac{(v|M_\beta|v'')(v''|M_\alpha|v')}{\omega_{v''v} - \omega + i\gamma} \ . \tag{3}$$

In this expression M_α is the crystal dipole moment operator, which possesses an expansion in powers of the displacements of the atoms from their equilibrium positions,

$$M_\alpha = \sum_{l\kappa\mu} M_{\alpha\mu}(l\kappa)\, u_\mu(l\kappa) + \tfrac{1}{2} \sum_{l\kappa\mu} \sum_{l'\kappa'\nu} M_{\alpha\mu\nu}(l\kappa; l'\kappa') u_\mu(l\kappa) \times u_\nu(l'\kappa') + \cdots \ . \tag{4}$$

In particular, the coefficients $[M_{\alpha\mu}(l\kappa)]$ are the transverse effective charges of the atoms, which govern the strength of the fundamental lattice absorption by the crystal. The damping constant γ is introduced into Eq. (3) to describe phenomenologically the anharmonic damping of the vibrational levels.

Combining Eqs. (2) and (3) we find that $i_{\alpha\gamma\beta\lambda}(\Omega)$ can be expressed equivalently as

$$i_{\alpha\gamma\beta\lambda}(\Omega) = \frac{1}{2\pi\hbar^2} \int_{-\infty}^{\infty} ds\, e^{-is\Omega} \int_0^\infty dt \int_0^\infty dt'\, e^{-i\omega t - \gamma t} e^{i\omega t' - \gamma t'} \times \langle [M_\lambda(s-t), M_\beta(s)][M_\alpha^+(0), M_\gamma^+(-t')] \rangle , \tag{5}$$

where the angular brackets $\langle\cdots\rangle$ denote an average with respect to the canonical ensemble described by the vibrational Hamiltonian corresponding to the electronic ground state of the crystal and $M_\alpha(t)$ is the dipole moment operator in the Heisenberg representation.

It follows directly from Eq. (5) that if the crystal has only a first-order dipole moment, and if the atomic vibrations are treated only in the harmonic approximation, then because in the harmonic approximation the commutator $[u_\alpha(l\kappa; t), u_\beta(l'\kappa'; t')]$ is a c-number function of $t-t'$, the expectation value in this equation is independent of s, and therefore there is no inelastic scattering of light. Consequently vibrational or electrical anharmonicity must be present in the crystal for the ionic Raman effect to take place.

In this paper we evaluate $i_{\alpha\gamma\beta\lambda}(\Omega)$ for a particular, simple kind of system of physical interest. We consider a crystal containing a number N_d of substitutional impurities, each of which occupies a site of T_d symmetry, and each of which gives rise to a triply degenerate localized vibration mode. We consider the ionic Raman scattering of light by these localized modes. The systems to which the present discussion applies include crystals of the zinc-blende structure containing substitutional impurities, e.g., GaAs: P. However, we will focus our attention on the case of CaF_2 containing H^- or D^- impurities (U centers) in the fluorine sublattice, because all of the parameters entering the theory are known from independent experiments.[2]

We base our calculation on several assumptions and approximations. The first is that the concentration of U centers is so low that we can obtain the total scattering cross section by multiplying the result for an isolated U center by the number of U centers. The second is that in a localized mode only the U center itself is vibrating. This seems to be a rather good approximation for the calculation of several properties of U centers in alkaline-earth fluorides.[2] The third is that we can restrict our attention to scattering at the absolute zero of temperature. This is also a reasonable assumption, because the high frequency of the localized mode (966 cm^{-1} for CaF_2: H^-) has the consequence that even room temperature can be considered a low temperature for the kinds of experiments we study here. Consequently, only down scattering (Stokes) spectra will be considered in this note.

The vibrational Hamiltonian for the U center can be written in the form

$$H = p^2/2M + \tfrac{1}{2}(M\omega_0^2)(x^2+y^2+z^2) + Lxyz + M_1(x^4+y^4+z^4) + M_2(x^2y^2+y^2z^2+z^2x^2) \qquad (6)$$

through quartic anharmonic terms. In this expression M is the mass of the U center, $\vec{p} = (p_x, p_y, p_z)$ is its momentum, and x, y, z are the Cartesian components of the displacement of the U center from its equilibrium position. The anharmonic terms will be regarded as a perturbation on the remainder of the Hamiltonian, which we denote by H_0,

$$H_0 = p^2/2M + \tfrac{1}{2}(M\omega_0^2)(x^2+y^2+z^2) \ . \qquad (7)$$

The eigenstates of H_0 can be represented by

$$|n_1n_2n_3\rangle = |n_1\rangle\,|n_2\rangle\,|n_3\rangle\ , \qquad (8)$$

where n_1, n_2, n_3 are any three non-negative integers,

$$|n_j\rangle = \left(\frac{\alpha}{\pi^{1/2}2^{n_j}n_j!}\right)^{1/2} H_{n_j}(\alpha x_j)\,e^{-(1/2)\alpha^2 x_j^2}\ ,$$

$$\alpha = (M\omega_0/\hbar)^{1/2} \quad , \qquad (9)$$

and $H_n(x)$ is the nth Hermite polynomial. The energy $E_{n_1n_2n_3}$ of the eigenstate $|n_1n_2n_3\rangle$ is

$$E_{n_1n_2n_3} = \tfrac{3}{2}\hbar\omega_0 + (n_1+n_2+n_3)\hbar\omega_0\ . \qquad (10)$$

The scattering processes we consider are those arising from the first-order dipole moment associated with the localized mode, which in the present case is given by

$$M_\alpha = e^* x_\alpha\ , \qquad (11)$$

where e^* is the transverse effective charge of the U center. The function $P_{\alpha\beta}^{vv'}(\omega)$ therefore takes the form

$$P_{\alpha\beta}^{vv'}(\omega) = (e^*)^2 \sum_{v''}\left(\frac{(v|x_\alpha|v'')\,(v''|x_\beta|v')}{\mathcal{E}_{v'',v'}+z} + \frac{(v|x_\beta|v'')\,(v''|x_\alpha|v')}{\mathcal{E}_{v'',v}-z}\right)\ , \qquad (12)$$

where $z = \hbar\omega - i\hbar\gamma$.

As a check on calculations based on Eq. (12) we note that for large $|z|$, $P_{\alpha\beta}^{vv'}(\omega)$ can be expanded in powers of $|z|^{-1}$ according to

$$P_{\alpha\beta}^{vv'}(\omega) = -(e^*)^2\left[\frac{1}{z^2}\,\frac{\hbar^2}{M}\,\delta_{\alpha\beta}\,\delta_{vv'} + \frac{1}{z^4}\,\frac{\hbar^4}{M^2}\left(v\left|\frac{\partial^2 v}{\partial x_\alpha \partial x_\beta}\right|v'\right) + O(z^{-4})\right]\ , \qquad (13)$$

where V represents the potential energy terms in the Hamiltonian, Eq. (6).

We denote by $|n_1n_2n_3)$ the eigenstate into which the state $|n_1n_2n_3\rangle$ goes in the presence of the anharmonic terms in the Hamiltonian (6), and the corresponding energy by $\mathcal{E}_{n_1n_2n_3}$. The calculation of the matrix elements $[(n_1n_2n_3|x_\alpha|n_1'n_2'n_3')]$ and the energies $\{\mathcal{E}_{n_1n_2n_3}\}$ is greatly simplified if we take as our unperturbed wave function not the $\{|n_1n_2n_3\rangle\}$ of Eqs. (8) and (9), but the $\frac{1}{2}n(n+1)$ linear combinations of these functions for a given $n = n_1+n_2+n_3$ which comprise basis functions for the irreducible representations of the point group T_d of the impurity site. These linear combinations and the corresponding energies $\{\mathcal{E}_{n_1n_2n_3}\}$ have been given by Elliott *et al.*[2] for $n = 0, 1, 2, 3$, and we shall make use of their results.

The first example we consider is scattering with a frequency shift equal to the fundamental vibrational transition frequency of the localized mode. We therefore require the matrix elements $P_{\alpha\beta}^{(000;100)}(\omega)$, $P_{\alpha\beta}^{(000;010)}(\omega)$, and $P_{\alpha\beta}^{(000;001)}(\omega)$. In calculating these quantities we will consider only vibrational transitions which yield matrix elements $(v|x_\alpha|v'')$ and $(v''|x_\beta|v')$ of which one is independent of the anharmonic coefficients L, M_1, and M_2, while the other is linear in L. Thus $P_{\alpha\beta}^{vv'}(\omega)$ will be linear in L, and higher-order anharmonic contributions will be neglected as small in comparison. The element of the tensor $P_{\alpha\beta}^{vv'}(\omega)$ we consider is

$$P_{xy}^{(000;001)}(\omega) = (e^*)\left(\frac{(000|x|011)(011|y|001)}{\mathcal{E}_{011;001}+z} + \frac{(000|y|101)(101|x|001)}{\mathcal{E}_{101;000}-z} + \frac{(000|x|100)(100|y|001)}{\mathcal{E}_{100;001}+z} + \frac{(000|y|010)(010|x|001)}{\mathcal{E}_{010;000}-z}\right) = -(e^*)^2\, 2L\left(\frac{\hbar}{2M\omega_0}\right)^{5/2} \frac{2\hbar^2\omega_0^2}{(\hbar\omega_0+z)(2\hbar\omega_0-z)z(\hbar\omega_0-z)} \; . \tag{14}$$

This result is in agreement with the expansion given by Eq. (13). In obtaining this element we have made the approximation of neglecting the anharmonic contributions to the transition frequencies $\omega_{v''v'}$ and $\omega_{v''v}$, inasmuch as the matrix elements

$$(000|x|011) = (000|y|101) = (\hbar/2M\omega_0)^2\,(2L/3\hbar\omega_0)$$

and

$$(100|y|001) = (010|x|001) = -(\hbar/2M\omega_0)^2\,(2L/\hbar\omega_0)$$

are already linear in L.

Combining these results with Eq. (2), we find that

$$i_{xyxy}(\Omega) = \left(\frac{e^*}{\hbar}\right)^4 4L^2\left(\frac{\hbar}{2M\omega_0}\right)^5 \times \frac{1}{[(\omega_0+\omega)^2+\gamma^2][(2\omega_0-\omega)^2+\gamma^2]} \times \frac{4\omega_0^4\delta(\Omega+\omega_0)}{(\omega^2+\gamma^2)[(\omega_0-\omega)^2+\gamma^2]} \; . \tag{15}$$

This tensor corresponds to scattering processes in which the incident light is polarized in the y direction and the scattered light is polarized in the x direction.

If we define the scattering efficiency $\mathcal{S}$ as the ratio of the power scattered into unit solid angle in the frequency interval $(\omega_s, \omega_s+d\omega_s)$ to the power incident on the crystal, we find that

$$\mathcal{S} = c_d l \frac{\omega_s^4}{c^4}\, i_{xyxy}(\Omega) \; , \tag{16}$$

$$\mathcal{S} = c_d l\left(\frac{e^*}{\hbar c}\right)^4 4L^2\left(\frac{\hbar}{2M\omega_0}\right)^5 \times \frac{1}{[(\omega_0+\omega)^2+\gamma^2][(2\omega_0-\omega)^2+\gamma^2]} \times \frac{4\omega_0^4(\omega-\omega_0)^4\,\delta(\Omega+\omega_0)}{(\omega^2+\gamma^2)[(\omega_0-\omega)^2+\gamma^2]} \; , \tag{17}$$

where c_d is the impurity concentration and l is the thickness of the crystal along the light path through it. To evaluate the coefficient of $\delta(\Omega+\omega_0)$ in this expression, which is the integrated intensity under the peak at $\Omega = -\omega_0$, we assume an impurity concentration $c_d = 10^{21}/\mathrm{cm}^3$,[3] $l = 1$ cm, $e^* = e$, the electronic charge, and the values of M, ω_0, and L appropriate to H$^-$ U-centers in CaF$_2$ at 20 °K.[2] A value of 1 cm^{-1} was chosen for γ, which is approximately the width associated with the fundamental and first harmonic of the localized mode at low temperatures. The variation of the integral of $\mathcal{S}$ over Ω with the frequency of the incident light ω in the neighborhood of the resonance at $\omega \approx 2\omega_0 = 1962.2$ cm^{-1} is plotted in Fig. 1. Inasmuch as a scattering efficiency of 10^{-8} or greater can be detected at the present time, even for scattered frequencies in the infrared, we see from this figure that for 1815 cm^{-1} $< \omega <$ 2110 cm^{-1} the scattering from localized modes with a frequency shift (downward) equal to the localized mode frequency should be observable. In particular, the use of a CO laser, which emits at wavelengths in the interval 5.2 μ to 6.0 μ (1923–1667 cm^{-1}),[4] as the source of incident light, should result in a resonance enhancement of the scattering efficiency.

The second scattering process we consider is the one in which the initial and final states $|v)$ and $|v')$ in Eq. (12) are the states $|000)$ and $|110)$, respectively. The shift in the frequency of the scattered light therefore is essentially twice the localized mode frequency. Of all possible intermediate states $|v'')$ we consider only those which yield contributions to $P_{xy}^{(000;110)}(\omega)$ which are of second order in L or of first order in M_1 and M_2. In this way we obtain the result that

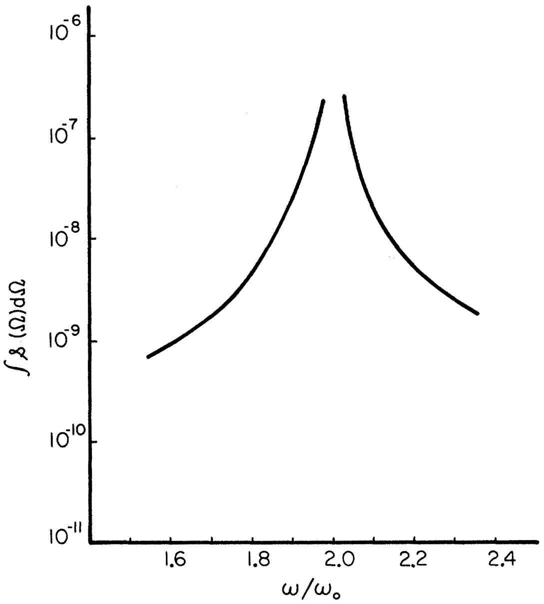

FIG. 1. Scattering efficiency for Raman scattering from the fundamental of the localized vibration modes due to H$^-$ U centers in CaF$_2$ is plotted as a function of the frequency of the incident light ($\omega_0 = 981.1$ cm^{-1}).

$$P_{xy}^{(000;110)}(\omega)=(e^*)^2\left(\frac{(000|x|100)(100|y|110)}{\mathcal{E}_{100;110}+z}+\frac{(000|y|010)(010|x|110)}{\mathcal{E}_{010;000}-z}+\frac{(000|x|011)(011|y|110)}{\mathcal{E}_{011;110}+z}\right.$$

$$\left.+\frac{(000|y|101)(101|x|110)}{\mathcal{E}_{101;000}-z}+\frac{(000|x|120)(120|y|110)}{\mathcal{E}_{120;110}+z}+\frac{(000|y|210)(210|x|110)}{\mathcal{E}_{210;000}-z}\right)\ . \tag{18}$$

In the harmonic approximation the first two terms of this expression cancel each other. Because the matrix elements in these terms are nonvanishing in the harmonic approximation, we have to obtain the anharmonic corrections to them in principle, as well as the anharmonic corrections to the transition energies in the denominators. In the remaining terms the matrix elements are of $O(L^2)$ or $O(M_{1,2})$, so that the transition energies in their denominators can be approximated by their values in the harmonic approximation. The nontrivial matrix elements entering Eq. (18) are found to be[5]

$$(000|x|100)=\left(\frac{\hbar}{2M\omega_0}\right)^{1/2}\left[1-\left(\frac{\hbar}{2M\omega_0}\right)^2\frac{12M_1+4M_2}{2\hbar\omega_0}+\left(\frac{\hbar}{2M\omega_0}\right)^3\frac{2L^2}{9(\hbar\omega_0)^2}\right]=(000|y|010)\ , \tag{19}$$

$$(100|y|110)=\left(\frac{\hbar}{2M\omega_0}\right)^{1/2}\left[1-\left(\frac{\hbar}{2M\omega_0}\right)^2\frac{12M_1+8M_2}{2\hbar\omega_0}+\left(\frac{\hbar}{2M\omega_0}\right)^3\frac{4L^2}{9(\hbar\omega_0)^2}\right]=(010|x|110), \tag{20}$$

$$(000|x|011)=\left(\frac{\hbar}{2M\omega_0}\right)^2\frac{2L}{3\hbar\omega_0}=(000|y|101)\ , \tag{21}$$

$$(011|y|110)=-\left(\frac{\hbar}{2M\omega_0}\right)^2\frac{2L}{\hbar\omega_0}=(101|x|110)\ , \tag{22}$$

$$(000|x|120)=\left(\frac{\hbar}{2M\omega_0}\right)^{5/2}\frac{\sqrt{2}M_2}{2\hbar\omega_0}+\left(\frac{\hbar}{2M\omega_0}\right)^{7/2}\frac{\sqrt{2}L^2}{6\hbar^2\omega_0^2}=(000|y|210)\ . \tag{23}$$

The required energy differences are[2]

$$\mathcal{E}_{110;100}=\hbar\omega_0+\left(\frac{\hbar}{2M\omega_0}\right)^2(12M_1+8M_2)-\frac{\hbar^2}{24M^3\omega_0^4}\,8L^2\ , \tag{24}$$

$$\mathcal{E}_{010;000}=\hbar\omega_0+\left(\frac{\hbar}{2M\omega_0}\right)^2(12M_1+4M_2)-\frac{\hbar^2}{24M^3\omega_0^4}\,4L^2\ . \tag{25}$$

Substitution of these expressions into Eq. (12) yields the result that to lowest nonvanishing order in the anharmonic force constants

$$P_{xy}^{(000;110)}(\omega)=(e^*)^2\left(\frac{\hbar}{2M\omega_0}\right)^3\times\frac{4\hbar^2\omega_0^2}{(\hbar\omega_0-z)^2(\hbar\omega_0+z)(3\hbar\omega_0-z)}\times\left(4M_2+\frac{L^2(z^2-2\hbar\omega_0 z+3\hbar^2\omega_0^2)}{3M\omega_0^2 z(z-2\hbar\omega_0)}\right)\ , \tag{26}$$

which satisfies Eq. (13). If, for simplicity, we neglect the small damping constant γ, we obtain for $i_{xyxy}(\Omega)$ in this case

$$i_{xyxy}(\Omega)=\left(\frac{e^*}{\hbar}\right)^4\left(\frac{\hbar}{2M\omega_0}\right)^6\frac{16\omega_0^4}{(\omega_0-\omega)^4(\omega_0+\omega)^2(3\omega_0-\omega)^2}\times\left(4M_2+\frac{L^2}{3M\omega_0^2}\ \frac{\omega^2-2\omega\omega_0+3\omega_0^2}{\omega(\omega-2\omega_0)}\right)^2\times\delta(\Omega+2\omega_0+\Delta\omega_{110;000})\ . \tag{27}$$

where[2]

$$\Delta\omega_{110;000}=\frac{\hbar}{(2M\omega_0)^2}(24M_1+12M_2)-\frac{\hbar}{24M^3\omega_0^4}\,12L^2. \tag{28}$$

The scattering efficiency for this process is given by

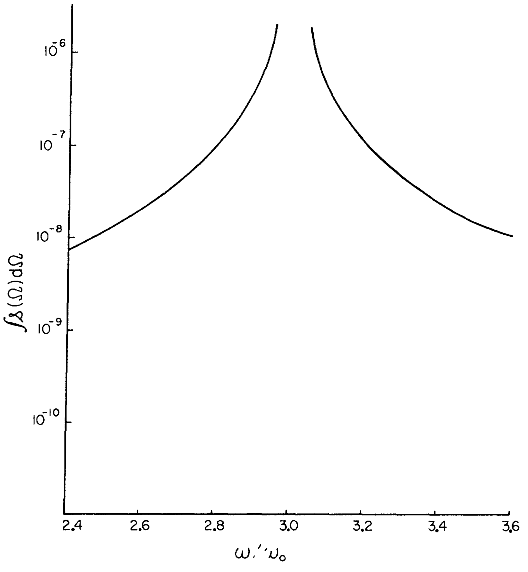

FIG. 2. Scattering efficiency for Raman scattering from the second harmonic of the localized vibration modes due to H⁻ U centers in CaF_2 is plotted as a function of the frequency of the incident light ($\omega_0=981.1\ cm^{-1}$).

$$\mathcal{S}=c_d l\left(\frac{e^*}{\hbar c}\right)^4\left(\frac{\hbar}{2M\omega_0}\right)^6\frac{16\omega_0^4}{(\omega_0-\omega)^4\,(\omega_0+\omega)^2\,(3\omega_0-\omega)^2}$$
$$\times\left(4M_2+\frac{L^2}{3M\omega_0^2}\,\frac{\omega^2-2\omega\omega_0+3\omega_0^2}{\omega(\omega-2\omega_0)}\right)^2$$
$$\times\,(\omega-2\omega_0-\Delta\omega_{110;000})^4\,\delta(\Omega+2\omega_0+\Delta\omega_{110;000})\,. \quad (29)$$

The variation of the integral of $\mathcal{S}$ over Ω with ω for $\omega > 2\omega_0 = 1962.2\ \mathrm{cm}^{-1}$ is plotted in Fig. 2 for the case of H^- *U*-centers in CaF_2. We see that the scattering efficiency for scattering with a frequency shift equal to the second harmonic of the localized mode frequency is an order of magnitude larger than it is for scattering with a frequency shift equal to the localized mode frequency. Due to the resonance enhancement of the scattering efficiency Eq. (29), for frequencies of the incident light in the vicinity of $3\omega_0$, scattering by this mechanism should be readily observable if a He-Ne laser which emits at $3.39\ \mu$ ($2950\ \mathrm{cm}^{-1}$) is used as the source of incident light.

It should be pointed out that the Hamiltonian describing the vibration of a *U* center in a crystal of the rocksalt or cesium chloride structure differs from that given by Eq. (6) only in that $L = 0$ in this case, because the impurity site is at the center of inversion symmetry. Consequently, the results of the present paper can be applied to the ionic Raman effect due to localized modes in such crystals by setting $L = 0$ wherever it appears.

The results of the present analysis indicate that the ionic Raman effect should be a useful tool for the experimental study of the vibrational properties of impurity atoms in crystals.

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*Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U.S. Air Force, under Grant No. AFOSR 68-1448A. The U. S. Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon.

[1] See for example, M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., New York, 1954), Sec. 19 and 20. The ionic Raman effect has also been described briefly by R. Loudon, Advan. Phys. 13, 423 (1964), in particular on p. 435, where it is stated that it is dominated by the electronic effect.

[2] R. J. Elliott, W. Hayes, G. D. Jones, H. F. Macdonald, and C. T. Sennett, Proc. Roy. Soc. (London) A289, 1 (1965).

[3] J. A. Harrington, R. T. Harley, and C. T. Walker, Solid State Commun. 8, 407 (1970).

[4] A. Mooradian (private communication).

[5] It should be noted that the result expressed by Eq. (23) differs from the result given by Eq. (6.9) of Ref. 2. If the latter result is used in Eq. (18), the resulting expression for $P_{xy}^{(000;110)}(\omega)$ does not agree with the general result, Eq. (13).