

Analysis of Raman Scattering by F Centers

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First-order Raman scattering has recently been measured by Worlock and Porto in NaCl and KCl colored with F centers. We carry out a quantum-mechanical calculation of the Raman cross section which shows that the frequency spectrum of phonons measured by Raman scattering is the same as the frequency spectrum of the phonons that broaden the F band. A lattice mode contributes to the Raman cross section in proportion to its contribution to the second moment of the F band. Our calculated value for the cross section, 2.0×10^{-24} cm², is in reasonable agreement with the measured value of the cross section, $\approx 5 \times 10^{-24}$ cm². The spin-orbit coupling in the first excited state of the F center, which also contributes to the broadening of the F band, causes Raman scattering in which there is a spin transition of the F center.

I. INTRODUCTION

THE F absorption band in alkali-halide crystals is several tenths of an electron-volt wide. From the interpretation of the temperature dependence of the absorption line shape, first measured by Pohl, it is known that the F band is broadened by lattice vibrations.¹⁻⁵ Over the years, however, very little experimental information has been obtained about the frequencies and symmetries of the lattice vibrations that broaden the F band.

Russell and Klick⁶ and later Konitzer and Markham⁷ fitted the temperature dependence of the half-width of the F band to a formula derived by Lax⁴ for the temperature dependence of $\langle E^2 \rangle$, the second moment or mean-square energy width of a phonon-broadened absorption band.

$$\langle E^2 \rangle \sim \coth(\hbar\omega_e/2kT).$$

These measurements yielded an effective phonon frequency ω_e which could be roughly interpreted as the average frequency of the lattice vibrations weighted according to their contribution to $\langle E^2 \rangle$.⁴

More recently, Henry, Schnatterly, and Slichter⁸ analyzed magneto-optical and stress experiments on the F band. They showed that the F band is broadened by vibrations of symmetry $\Gamma_1, \Gamma_3, \Gamma_5$ and by the spin-orbit coupling in the p -like (Γ_4) first excited state of the F center. These four interactions contribute additively to the second moment, which may be written as

$$\langle E^2 \rangle = \langle E^2 \rangle_1 + \langle E^2 \rangle_3 + \langle E^2 \rangle_5 + \langle E^2 \rangle_{so}. \quad (1)$$

In Schnatterly's stress experiments, the first three terms in Eq. (1) were evaluated for a number of alkali-halide crystals.⁹ $\langle E^2 \rangle_{so}$ has been determined in various alkali

halides by the magneto-optical experiments of Mort, Lüty, and Brown,¹⁰ of Margerie and Romestain,^{11,12} and of Gareyte and d'Aubigné.¹³

Much more detailed information about the lattice frequencies has come recently from Raman-scattering measurements. Acting on a suggestion of Kleinman,¹⁴ Worlock and Porto¹⁵ measured first-order Raman scattering in NaCl and KCl crystals heavily colored with F centers. An example of their data for NaCl is shown in Fig. 1. They found a continuous spectrum of frequencies which contribute to first-order Raman scattering. The vibrations causing the Raman scattering must affect the F center, because in a pure alkali-halide crystal, not containing F centers, there is no first-order Raman scattering. However, it is not clear from their data to

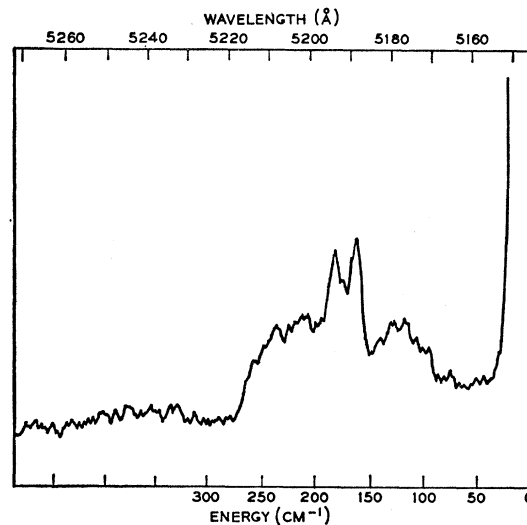


Fig. 1. Raman scattering in NaCl colored with F centers. This spectrum was measured by J. M. Worlock and S. P. S. Porto using a 5154-Å argon-ion laser.

¹⁰ J. Mort, F. Lüty, and F. C. Brown, *Phys. Rev.* **137**, A566 (1965).

¹¹ J. Margerie and R. Romestain, *Compt. Rend.* **258**, 4490 (1964).

¹² R. Romestain and J. Margerie, *Compt. Rend.* **258**, 2525 (1964).

¹³ J. Gareyte and Merle d'Aubigné, *Compt. Rend.* **258**, 6393 (1964).

¹⁴ D. A. Kleinman, *Phys. Rev.* **134**, 423 (1964).

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

¹ R. W. Pohl, *Proc. Phys. Soc. (London)* **A167**, 384 (1937).

² R. W. Gurney and N. F. Mott, *Trans. Faraday Soc.* **35**, 69 (1939).

³ S. I. Pekar, *Zh. Eksperim. i Teor. Fiz.* **20**, 510 (1950); **22**, 641 (1952).

⁴ M. Lax, *J. Chem. Phys.* **20**, 1752 (1952).

⁵ R. C. O'Rourke, *Phys. Rev.* **91**, 265 (1953).

⁶ G. A. Russell and C. C. Klick, *Phys. Rev.* **101**, 1473 (1956).

⁷ J. Konitzer and J. Markham, *J. Chem. Phys.* **32**, 843 (1960).

⁸ C. H. Henry, S. E. Schnatterly, and C. P. Slichter, *Phys. Rev.* **137**, A583 (1965).

⁹ S. E. Schnatterly, *Phys. Rev.* **140**, A1364 (1965).

what extent the vibrations which cause Raman scattering also broaden the F band.

In this paper we make an approximate calculation of the cross section for first-order Raman scattering due to the presence of F centers. We find that a given vibration contributes to Raman scattering in proportion to how much it contributes to $\langle E^2 \rangle$. Thus, the spectrum of frequencies measured by Worlock and Porto is just the spectrum of frequencies of the phonons which broaden the F band.

Furthermore, we shall show that the spin-orbit interaction which contributes to the broadening of the F band also causes Raman scattering. The spin-orbit interaction causes Raman scattering in which there is a spin transition instead of a lattice transition. The Raman scattering cross section for a spin transition is related to $\langle E^2 \rangle_{so}$ in nearly the same manner that the Raman scattering for a lattice transition is related to $\langle E^2 \rangle_1 + \langle E^2 \rangle_3 + \langle E^2 \rangle_5$.

In Sec. II, we discuss the physical mechanisms for Raman scattering and point out the difference between our mechanism and the one discussed by Kleinman.¹⁴

In Sec. III, we carry out a quantum-mechanical calculation of the Raman scattering cross sections using the same methods that Henry, Schnatterly, and Slichter employed to calculate the moments of the F band. We compare our numerical results for the total cross section with the measurements of Worlock and Porto, and find reasonable agreement. A relation between the angular Raman cross sections and the total Raman cross section, which we use in Sec. III, is derived in the Appendix.

II. PHYSICAL MECHANISMS

A. Raman Scattering by Lattice Vibrations

In this section, for simplicity, let us treat the F center as a singlet-to-singlet transition coupled to a single lattice coordinate Q . The polarizability of the F center $\alpha(Q)$ is given by

$$\alpha(Q) = M(Q)^2 \left(\frac{\mathcal{E}_{10c}}{\mathcal{E}} \right)^2 \frac{2E(Q)}{E^2(Q) - E^2}, \quad (2)$$

where $M(Q)$ is the electric-dipole matrix element between the ground state and the excited state $E(Q)$ is the transition energy, and $(\mathcal{E}_{10c}/\mathcal{E})^2$ is the local-field correction. As Q varies at frequency ω_q , the scattered light will be amplitude-modulated, and hence will have side bands at $\omega \pm \omega_q$. The cross section for Raman scattering into both side bands is easily shown to be

$$\sigma = (8\pi/3) [E^4/(\hbar c)^4] \langle (\Delta\alpha)^2 \rangle; \quad (3)$$

$\langle (\Delta\alpha)^2 \rangle$ is the mean-square-change in α . $\Delta\alpha$ is given by the derivative of Eq. (2).

$$\Delta\alpha = \bar{\alpha} \left[\frac{\Delta(M(Q)^2)}{M^2} + \frac{\bar{E}^2 + E^2}{\bar{E}^2 - E^2} \frac{\Delta E(Q)}{\bar{E}} \right], \quad (4)$$

where $\bar{\alpha}$ is the average polarizability and \bar{E} is the average transition energy. The change in M^2 results from the perturbation of the lattice distortion mixing other higher excited states of the F center into the ground state and first excited state. In this paper, we are neglecting the mixing of nondegenerate states (configuration mixing) and thus are neglecting the first term in Eq. (4). This is justified in our calculations because we are concerned with the near-resonance case where $\bar{E} - E \ll \bar{E}$, which is precisely the condition for which Raman scattering has been observed.¹⁵ For this case, we expect the second term in Eq. (4) to dominate. We can estimate the relative magnitude of the two terms as follows. The oscillator strength of the F center is nearly unity and should vary very slowly as Q varies. If we take the oscillator strength

$$f = 2E(Q)M^2(Q)(m/e^2\hbar^2) \quad (5)$$

to be approximately constant, we have

$$\Delta M^2/M^2 \approx -\Delta E/\bar{E}. \quad (6)$$

Hence the second term in Eq. (4) is clearly dominant near resonance. Furthermore, Kleinman's¹⁴ estimate of σ , which takes into account only the first term in Eq. (4), gives a scattering cross section about 30 times smaller than our estimate for the near resonance Raman-scattering experiments of Worlock and Porto.¹⁵ Substituting the second term of Eq. (4) into Eq. (3), we find

$$\sigma_{\text{latt}} = \sigma_T f^2 \left(\frac{\mathcal{E}_{10c}}{\mathcal{E}} \right)^4 \frac{E^4 (\bar{E}^2 + E^2)^2}{\bar{E}^2 (\bar{E}^2 - E^2)^4} \langle E^2 \rangle_{\text{latt}}, \quad (7)$$

where $\sigma_T = (8\pi/3)(e^2/mc^2)^2$ is the Thompson scattering cross section for scattering light by a free electron and $\langle E^2 \rangle_{\text{latt}} = \langle \Delta E(Q)^2 \rangle$ is the contribution to the second moment of the F band due to the lattice vibration Q . The quantum-mechanical calculation of σ_{latt} discussed in the next section results in a formula *identical* to Eq. (7).

B. Raman Scattering by Spins

The large spin-orbit coupling in the excited states of F centers in the heavy alkali halides results in a large paramagnetic Faraday rotation. Paramagnetic Faraday rotation of z -polarized light into x -polarized light is induced by an off-diagonal component of the polarizability tensor α_{zx} proportional to the spin-orbit coupling constant λ for the excited state and to the component of spin in the y direction S_y . If a magnetic field \mathbf{H} is applied in the z direction, \mathbf{S} will precess around \mathbf{H} at the Zeeman frequency ω_H . This will cause an amplitude modulation of α_{zx} at ω_H and will result in Raman scattering at $\omega \pm \omega_H$. The Raman scattering will be depolarized and proportional to $\lambda^2 \langle S_y^2 \rangle = \frac{1}{4} \lambda^2$. $\langle E^2 \rangle_{so}$ is also proportional to λ^2 so that

$$\sigma_{\text{spin}} = C' \langle E^2 \rangle_{so}, \quad (8)$$

just as

$$\sigma_{\text{latt}} = C \langle E^2 \rangle_{\text{latt}}. \quad (9)$$

In the next section we will see that the proportionality constants C and C' in Eqs. (8) and (9) are nearly identical.

The Raman scattering results in a transition in which the F center spin flips in a magnetic field. The width of the Raman line is just the width of the electron-spin resonance line of the F center, about $5 \times 10^{-3} \text{ cm}^{-1}$ (50 G).

III. THEORY

We will now show that the various vibrational modes and the spin-orbit interaction contribute to the total Raman-scattering cross section in direct proportion to the extent that these interactions contribute to the second moment of the F band. We shall make a quantum-mechanical calculation of the Raman cross section, and relate our result to the expression for the second moment of the F band calculated by Henry, Schnatterly, and Slichter (HSS).⁸ The methods and approximations used in this calculation are very similar to those used by HSS to calculate the moments of the F band. The interested reader is urged to consult their paper.

Optical absorption and Raman scattering by F centers both take place through an electric-dipole interaction given by

$$\mathcal{H}_{\text{rad}} = - \left(\frac{\mathcal{E}_{\text{loc}}}{\mathcal{E}} \right) P_{\eta} E_{\eta}(\vec{x}, t). \quad (10)$$

($\mathcal{E}_{\text{loc}}/\mathcal{E}$) is the local field correction, E_{η} is the electric field of polarization η , and P_{η} is the electric dipole-moment operator of the F -center electron in direction \hat{e}_{η} .

HSS write the optical absorption line shape of the F band as

$$f_{\eta}(E) = \text{av}_a \sum_b |\langle b | P_{\eta} | a \rangle|^2 \delta(E_b - E_a - E); \quad (11)$$

$|a\rangle$ are the ground states and $|b\rangle$ are the first excited states of the F center including the spin and lattice coordinates. HSS define the moments of the F band as

$$\begin{aligned} A &= \int f_{\eta}(E) dE = \text{av}_a \sum_b |\langle b | P_{\eta} | a \rangle|^2, \\ \bar{E} &= A^{-1} \int f_{\eta}(E) E dE = A^{-1} \text{av}_a \\ &\quad \times \sum_b |\langle b | P_{\eta} | a \rangle|^2 (E_b - E_a), \\ \langle E^2 \rangle &= A^{-1} \int f_{\eta}(E) E^2 dE = A^{-1} \text{av}_a \sum_b |\langle b | P_{\eta} | a \rangle|^2 (E_b - E_a - \bar{E})^2. \end{aligned} \quad (12)$$

A is the zeroth moment or area, \bar{E} is the first moment or mean energy, and $\langle E^2 \rangle$ is the normalized second moment of the F band measured about \bar{E} .

The angular cross section for light of incident polarization η and scattered polarization η' is given by

$$\begin{aligned} \frac{d\sigma}{d\Omega} \eta' \eta &= \left(\frac{\mathcal{E}_{\text{loc}}}{\mathcal{E}} \right)^4 \frac{E_L E_S^3}{(\hbar c)^4} \text{av}_a \\ &\quad \times \sum_{a' \neq a} \left| \sum_b \left\{ \frac{\langle a' | P_{\eta'} | b \rangle \langle b | P_{\eta} | a \rangle}{E_b - E_a - E_L} \right. \right. \\ &\quad \left. \left. + \frac{\langle a' | P_{\eta} | b \rangle \langle b | P_{\eta'} | a \rangle}{E_b - E_a + E_S} \right\} \right|^2, \quad (13) \end{aligned}$$

where E_L and E_S are the energies of the incident and scattered light.¹⁶

We will make the following simplifying assumptions:

(a) We can neglect transitions to higher excited states of the F center which give rise to the K band and Lüty bands since these transitions have low oscillator strengths.

(b) We neglect the difference in energy between E_L and E_S , writing

$$E_L \approx E_S = E. \quad (14)$$

(c) We expand the denominator in Eq. (4) about \bar{E}

$$\frac{1}{E_b - E_a \mp E} \approx \frac{1}{\bar{E} \mp E} - \frac{E_b - E_a - \bar{E}}{(\bar{E} \mp E)^2} + \dots \quad (15)$$

(d) We neglect mixing of the nondegenerate electronic states (configuration mixing) by the spin-orbit interaction and electron-lattice interaction. This is equivalent to neglecting the modulation of M^2 by the lattice, discussed in Sec. II.

(e) We take the electron-lattice interaction to be linear in the lattice coordinates.

Assumptions (d) and (e) were made by HSS in computing the moments of the F band.

We wish to compute σ , the total cross section. In the Appendix we show that σ is independent of the incident polarization and is given by

$$\sigma = \frac{8\pi}{3} \sum_k \left(\frac{d\sigma}{d\Omega} kx \right). \quad (16)$$

Substituting Eqs. (14), (15), and (16) into Eq. (13) gives

$$\begin{aligned} \sigma &= \left(\frac{8\pi}{3} \right) \left(\frac{\mathcal{E}_{\text{loc}}}{\mathcal{E}} \right)^4 \left(\frac{E}{\hbar c} \right)^4 \text{av}_a \\ &\quad \times \sum_{a' \neq a} \sum_k \left| \sum_b \left\{ \frac{\langle a' | P_k | b \rangle \langle b | P_x | a \rangle}{(\bar{E} - E)^2} (E_b - E_a - \bar{E}) \right. \right. \\ &\quad \left. \left. + \frac{\langle a' | P_x | b \rangle \langle b | P_k | a \rangle}{(\bar{E} + E)^2} (E_b - E_a - \bar{E}) \right\} \right|^2. \quad (17) \end{aligned}$$

¹⁶ W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, London, 1954), p. 192.

Only the second term in Eq. (15) appears in Eq. (17). The first term of Eq. (15) can easily be shown not to contribute to σ because $|a'\rangle$ is different from $|a\rangle$.

Following HSS, we write the Hamiltonian of the F center as

$$\mathcal{H} = \mathcal{H}_E(\mathbf{r}) + \mathcal{H}_{e1}(\mathbf{r}, Q) + \mathcal{H}_L(Q) + \mathcal{H}_{so}(\mathbf{r}, \mathbf{S}). \quad (18)$$

$$\mathcal{H}_E = (\mathbf{p})^2/2m + V(\mathbf{r}) \quad (19)$$

is the electronic Hamiltonian of the F center, neglecting spin-orbit coupling and with the lattice fixed at $Q=0$, the equilibrium position it possesses with the center in its orbital ground state. The eigenstates of $\mathcal{H}_E(\mathbf{r})$ include an s -like (Γ_1) orbital ground state $|\alpha(\mathbf{r})\rangle$, a p -like (Γ_4) 3-fold degenerate orbital excited state $|\beta_i(\mathbf{r})\rangle$,

$$\begin{aligned} &= |x\rangle \quad i=1, \\ |\beta_i\rangle &= |y\rangle \quad i=2, \\ &= |z\rangle \quad i=3, \end{aligned} \quad (20)$$

and other higher excited states $|\gamma_i(\mathbf{r})\rangle$, etc., multiplied by the spin-wave function $|m\rangle$.

$$\mathcal{H}_L(Q) = \sum_{\alpha ar} \left(\frac{P_{\alpha ar}^2}{2M_{\alpha r}} + \frac{1}{2} M_{\alpha r} \omega_{\alpha r}^2 Q_{\alpha ar}^2 \right) \quad (21)$$

is the lattice Hamiltonian computed with the F center in its orbital ground state $|\alpha\rangle$. The normal coordinates $Q_{\alpha ar}$ are classified according to symmetry. $Q_{\alpha ar}$ transforms like the a th basis vector of the irreducible representation Γ_α . The subscript r labels the different normal modes of symmetry Γ_α . The lattice wave functions will be denoted as $|l\rangle$, where

$$\mathcal{H}_L|l\rangle = E_l|l\rangle. \quad (22)$$

$|l\rangle$ is a product of harmonic oscillator wave functions. \mathcal{H}_{e1} is the electron lattice interaction. It is assumed to be linear in Q and of the form

$$\mathcal{H}_{e1}(\mathbf{r}, Q) = \sum_{\alpha ar} V_{\alpha ar}(\mathbf{r}) Q_{\alpha ar}. \quad (23)$$

This interaction alters the equilibrium position of the lattice when the F center is in an excited state. The ground-state lattice equilibrium position is $Q=0$, so that we require

$$\langle \alpha | V_{\alpha ar} | \alpha \rangle = 0. \quad (24)$$

The spin-orbit interaction \mathcal{H}_{so} will be taken simply as

$$\mathcal{H}_{so} = \lambda \mathbf{L} \cdot \mathbf{S} = \lambda \sum_\gamma L_\gamma S_\gamma. \quad (25)$$

For the orbital singlet state $|\alpha\rangle$

$$\langle \alpha | \mathbf{L} | \alpha \rangle = 0. \quad (26)$$

The ground state $|a\rangle$ is taken as

$$|a\rangle = |\alpha\rangle |m\rangle |l\rangle, \quad (27)$$

a product of the orbital wave function $|\alpha\rangle$ and the complete set of spin states $|m\rangle$, and a complete set of

lattice states $|l\rangle$. HSS point out that the excited state $|b\rangle$ cannot be written as a simple product $|\beta_i\rangle |m\rangle |l\rangle$ because of the mixing of such states by H_{so} and H_{e1} . Instead, they take the excited states $|b\rangle$ to be a linear combination of the products $|\beta_i\rangle |m\rangle |l\rangle$ for which \mathcal{H} is diagonal. That is

$$\langle b' | \mathcal{H}_E + \mathcal{H}_L + \mathcal{H}_{e1} + \mathcal{H}_{so} | b \rangle = E_b \delta_{bb'}. \quad (28)$$

HSS show that

$$\bar{E} = \langle b | \mathcal{H}_E | b \rangle - \langle a | \mathcal{H}_E | a \rangle, \quad (29)$$

and that

$$\begin{aligned} (E_b - E_a - \bar{E}) &= \langle b | \mathcal{H} - \mathcal{H}_E | b \rangle - \langle a | \mathcal{H} - \mathcal{H}_E | a \rangle \\ &= \langle b | \mathcal{H}_{e1} + \mathcal{H}_{so} + \mathcal{H}_L | b \rangle - \langle a | \mathcal{H}_L | a \rangle \\ &= \langle b | \mathcal{H}_{e1} + \mathcal{H}_{so} + \mathcal{H}_L - E_l | b \rangle. \end{aligned} \quad (30)$$

Using Eq. (30), the sums of the type encountered in Eq. (17) can now be easily evaluated. Consider the first sum, which we will call S . S can be rewritten as

$$\begin{aligned} S &= \sum_b \langle a' | P_k | b \rangle \langle b | P_x | a \rangle (E_b - E_a - \bar{E}) \\ &= \sum_{bb'} \langle a' | P_k | b \rangle \langle b | \mathcal{H}_{e1} + \mathcal{H}_{so} \\ &\quad + \mathcal{H}_L - E_l | b' \rangle \langle b' | P_x | a \rangle. \end{aligned} \quad (31)$$

We are able to sum independently over b and b' because the operator $\mathcal{H}_{e1} + \mathcal{H}_{so} + \mathcal{H}_L$ is diagonal in the states $|b\rangle$. The exact states $|b\rangle$ are a linear combination of the products $|\beta_i\rangle |m\rangle |l\rangle$. According to the principle of spectroscopic stability employed at length by HSS,

$$\begin{aligned} \sum_b |b\rangle \langle b| &= \sum_i |\beta_i\rangle \langle \beta_i| \sum_m |m\rangle \langle m| \sum_l |l\rangle \langle l| \\ &= \sum_i |\beta_i\rangle \langle \beta_i|. \end{aligned} \quad (32)$$

Equation (31) reduces to

$$\begin{aligned} S &= \sum_{ij} \langle l' m' | \langle \alpha | P_k | \beta_i \rangle \langle \beta_i | \mathcal{H}_{so} + \mathcal{H}_{e1} + \mathcal{H}_L - E_l | \beta_j \rangle \\ &\quad \times \langle \beta_j | P_x | \alpha \rangle | l m \rangle. \end{aligned} \quad (33)$$

The matrix elements $\langle \alpha | P_k | \beta_i \rangle$ are related by

$$\langle \alpha | P_k | \beta_i \rangle = \langle \alpha | P_x | x \rangle \delta_{ki}. \quad (34)$$

Using

$$(\mathcal{H}_L - E_l) | l \rangle = 0, \quad (35)$$

Eq. (33) reduces to

$$\begin{aligned} S &= \langle \alpha | P_x | x \rangle^2 \langle l' m' | \langle \beta_k | \mathcal{H}_{so} + \mathcal{H}_{e1} | x \rangle | l m \rangle \\ &= \langle \alpha | P_x | x \rangle^2 \left[\sum_{\alpha ar} \langle \beta_k | V_{\alpha ar} | x \rangle \langle l' | Q_{\alpha ar} | l \rangle \langle m' | m \rangle \right. \\ &\quad \left. + \lambda \sum_\gamma \langle \beta_k | L_\gamma | x \rangle \langle l' | l \rangle \langle m' | S_\gamma | m \rangle \right]. \end{aligned} \quad (36)$$

For lattice Raman scattering, $l' \neq l$ and $m' = m$. σ_{latt} is found by substitution of Eq. (36) into Eq. (17). In evaluating Eq. (17), we can drop the condition $l' \neq l$ because

$$\langle l | Q_{\alpha ar} | l \rangle = 0. \quad (37)$$

Using

$$\langle \beta_k | V_{aar} | x \rangle = \langle x | V_{aar} | \beta_k \rangle, \quad (38)$$

and

$$\begin{aligned} \text{av}_a \sum_{l'} \langle l' | Q_{aar} | l \rangle^* \langle l' | Q_{a'a'r'} | l \rangle \\ = \text{av}_a \langle l | Q_{aar} Q_{a'a'r'} | l \rangle = \langle Q_{aar}^2 \rangle \delta_{aa'} \delta_{aa'} \delta_{rr'} \end{aligned} \quad (39)$$

$$\text{gives } \sigma_{\text{latt}} = C \sum_{a\alpha r k} \langle x | V_{aar} | \beta_k \rangle \langle \beta_k | V_{aar} | x \rangle \langle Q_{aar}^2 \rangle, \quad (40)$$

$$C = \sigma_T f^2 \left(\frac{\mathcal{E}_{\text{loc}}}{\mathcal{E}} \right)^4 \frac{E^4 (\bar{E}^2 + E^2)^2}{\bar{E}^2 (\bar{E}^2 - E^2)^4}, \quad (41)$$

where σ_T is the Thompson scattering cross section defined in the last section, and f is the oscillator strength given by

$$f = (2m/e^2 \hbar^2) \langle x | P_x | \alpha \rangle^2 \bar{E}. \quad (42)$$

HSS show that vibrations of symmetry Γ_1 , Γ_3 , and Γ_5 , and the spin-orbit interaction contribute additively to the second moment, which can be written (in our notation) as

$$\begin{aligned} \langle E^2 \rangle = \sum_{a\alpha r k} \langle x | V_{aar} | \beta_k \rangle \langle \beta_k | V_{aar} | x \rangle \langle Q_{aar}^2 \rangle \\ + \lambda^2 \sum_{\gamma k} \langle x | L_\gamma | \beta_k \rangle \langle \beta_k | L_\gamma | x \rangle \langle S_\gamma^2 \rangle \\ = \langle E^2 \rangle_{\text{latt}} + \langle E^2 \rangle_{\text{so}}. \end{aligned} \quad (43)$$

Thus we may write Eq. (41) compactly as

$$\sigma_{\text{latt}} = C \langle E^2 \rangle_{\text{latt}}. \quad (44)$$

In the exact same manner we can evaluate the Raman cross section for a spin transition. In this case $m' \neq m$ and $l' = l$. Using

$$\langle \beta_k | L_\gamma | x \rangle = - \langle x | L_\gamma | \beta_k \rangle, \quad (45)$$

and assuming that the spins are quantized by a magnetic field along some arbitrary direction gives

$$\sigma_{\text{spin}} = C' \langle E^2 \rangle_{\text{so}}, \quad (46)$$

$$C' = \left[\sigma_T f^2 \left(\frac{\mathcal{E}_{\text{loc}}}{\mathcal{E}} \right)^4 \frac{4E^6}{(\bar{E}^2 - E^2)^4} \right] = C \frac{4\bar{E}^2 E^2}{(\bar{E}^2 + E^2)^2}. \quad (47)$$

Comparison of Eqs. (40) and (43) shows that a given lattice mode contributes to first-order Raman scattering in direct proportion to its contribution to the second moment of the F band. For NaCl, using the 5145-Å argon-ion laser line $\langle E^2 \rangle_{\text{latt}} = 1.35 \times 10^{-2} (\text{eV})^2$, $\bar{E} = 2.762$ eV, $E = 2.410$ eV, $f = 0.81$, $\sigma_T = (0.665)10^{-24}$ cm², and $(\mathcal{E}_{\text{loc}}/\mathcal{E})^4 = [\frac{1}{3}(n^2 + 2)]^4 = 4.63$. This leads to

$$\sigma_{\text{latt}} = (1.98)10^{-24} \text{ cm}^2.$$

Worlock and Porto¹⁷ found experimentally for NaCl that

$$\sigma \approx 5 \times 10^{-24} \text{ cm}^2.$$

¹⁷ J. M. Worlock and S. P. S. Porto (unpublished).

In view of the admitted inaccuracies in their measurement of the absolute Raman cross section, this agreement is reasonable.

For E near \bar{E} , we see from Eq. (48) that $C \approx C'$. For this case we have

$$\frac{\sigma_{\text{spin}}}{\sigma_{\text{latt}}} \approx \frac{\langle E^2 \rangle_{\text{so}}}{\langle E^2 \rangle_{\text{latt}}}. \quad (48)$$

For the light alkali halides such as NaCl, the spin-orbit interaction is small and

$$(\sigma_{\text{spin}}/\sigma_{\text{latt}})_{\text{NaCl}} \approx 10^{-3}.$$

For a heavy alkali halide like CsCl, the spin-orbit interaction is much larger and

$$\sigma_{\text{spin}}/\sigma_{\text{latt}} \approx 10^{-1}.$$

In Raman scattering by spins, the Raman linewidth is the ESR linewidth (50 G). In a field of 30 kG, the Q of the Raman line would be 600 and Raman scattering should be detectable. Raman scattering by a spin transition has been discussed by a number of authors.¹⁸⁻²⁰ However, there are no experimental observations as yet for any system.

We could go on to calculate the various angular cross sections directly from Eq. (12). This is unnecessary, however, because for vibrations of a given symmetry Γ_α , the various angular cross sections $[(d\sigma/d\Omega)\eta'\eta]_\alpha$ are related to each other by Raman tensors which may be calculated directly from group theory.

$$((d\sigma/d\Omega)\eta'\eta)_\alpha = C_\alpha |\sum_a \hat{e}_{\eta'} \cdot \mathbf{T}_{\alpha a} \cdot \hat{e}_\eta|^2. \quad (49)$$

These tensors $\mathbf{T}_{\alpha a}$ have been tabulated by Loudon²¹ for the various point group symmetries. The Raman tensors for vibrations of symmetry Γ_1 , Γ_3 , Γ_5 , and for the spin-orbit interaction are tabulated in Fig. 2. The result of our calculation is that the constants of proportionality C_α are directly related to $\langle E^2 \rangle_\alpha$ and may be evaluated using

$$\frac{8\pi}{3} \sum_k \left(\frac{d\sigma_{kz}}{d\Omega} \right)_\alpha = \sigma_\alpha = C' \langle E^2 \rangle_\alpha, \quad \alpha = 1, 3, 5. \quad (50)$$

Equation (50) follows from Eqs. (16) and (41). Using Eqs. (49) and (50) we find for example

$$\begin{aligned} ((d\sigma/d\Omega)100,100)_{\text{latt}} &= (3/8\pi)C[\langle E^2 \rangle_1 + \langle E^2 \rangle_3], \\ ((d\sigma/d\Omega)001,100)_{\text{latt}} &= (3/8\pi)C[\frac{1}{2}\langle E^2 \rangle_5], \\ ((d\sigma/d\Omega)1\bar{1}0,110)_{\text{latt}} &= (3/8\pi)C[\frac{3}{4}\langle E^2 \rangle_3]. \end{aligned} \quad (51)$$

The subscripts 100, $\bar{1}\bar{1}0$, etc., refer to the direction in the crystal of the polarization of the incident light and scat-

¹⁸ R. J. Elliott and R. Loudon, Phys. Letters 3, 189 (1963).

¹⁹ Y. R. Shen and N. Bloembergen, Phys. Rev. 143, 372 (1966).

²⁰ P. S. Pershan, J. P. von det Ziel, and L. D. Malmstrom, Phys. Rev. 143, 574 (1966).

²¹ R. Loudon, Advan. Phys. 13, 423 (1964), 14, 621(E) (1965).

IRREDUCIBLE REPRESENTATION	BASIS FUNCTION	RAMAN TENSOR
Γ_1	$x^2 + y^2 + z^2$	$\begin{pmatrix} 1 & & & \\ & 1 & & \\ & & 1 & \\ & & & 1 \end{pmatrix}$
Γ_3	$2z^2 - x^2 - y^2$	$\begin{pmatrix} -1 & & & \\ & -1 & & \\ & & & 2 \end{pmatrix}$
	$\sqrt{3}(x^2 - y^2)$	$\begin{pmatrix} \sqrt{3} & & & \\ & -\sqrt{3} & & \\ & & & \end{pmatrix}$
Γ_5	yz	$\begin{pmatrix} & & & \\ & & & \\ & & & 1 \\ & & 1 & \end{pmatrix}$
	zx	$\begin{pmatrix} & & & \\ & & & \\ & & & 1 \\ 1 & & & \end{pmatrix}$
	xy	$\begin{pmatrix} & & & \\ & & & \\ & & & \\ 1 & & & \end{pmatrix}$
	L_x	$\begin{pmatrix} & & & \\ & & & \\ & & & i \\ & & -i & \end{pmatrix}$
Γ'_4	L_y	$\begin{pmatrix} & & & \\ & & & \\ & & & -i \\ i & & & \end{pmatrix}$
	L_z	$\begin{pmatrix} & & & \\ & & & \\ & & & \\ -i & & & i \end{pmatrix}$

FIG. 2. The basis functions and Raman tensors for the vibrations of symmetry Γ_1 , Γ_3 , and Γ_5 and for the spin-orbit interaction of symmetry Γ'_4 .

tered light. Measurements of these three angular cross sections would allow a determination of the relative sizes of $\langle E^2 \rangle_1$, $\langle E^2 \rangle_3$, and $\langle E^2 \rangle_5$. These quantities have already been measured by Schnatterly⁹ for a number of different alkali-halide crystals. Such measurements would allow a check of the ideas presented in this paper.

Computation of the angular cross sections for the spin case, with the magnetic field in the [001] direction, shows that

$$\begin{aligned} ((d\sigma/d\Omega)100,100)_{\text{spin}} &= 0, \\ ((d\sigma/d\Omega)001,100)_{\text{spin}} &= (3/8\pi)C^{1/2}\langle E^2 \rangle_{\text{so}}. \end{aligned} \quad (52)$$

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APPENDIX: RELATION BETWEEN THE TOTAL AND ANGULAR CROSS SECTIONS

The combined effect of the incident electric field E_η and a lattice coordinate Q is to produce a nonlinear polarization of the medium \mathbf{P} . $((d\sigma/d\Omega)\eta'\eta)$ will be proportional to the $P_{\eta'}^2$.

$$((d\sigma/d\Omega)\eta'\eta) = CP_{\eta'}^2. \quad (A1)$$

The total light scattered in direction \hat{r} will be proportional to the squared amplitude of the component of \mathbf{P} perpendicular to \hat{r} . Hence

$$\begin{aligned} \sigma &= C \int d\Omega [\mathbf{P}^2 - (\mathbf{P} \cdot \hat{r})^2] \\ &= (8\pi/3)C\mathbf{P}^2 \\ &= \frac{8\pi}{3} \sum_k \left(\frac{d\sigma}{d\Omega} \right)_{k\eta}. \end{aligned} \quad (A2)$$

We will now show that σ is independent of η . For vibrations of symmetry Γ_α , \mathbf{P} is given by

$$\mathbf{P} = \sum_a \mathbf{T}_{\alpha a} Q_{\alpha a} \cdot \hat{e}_\eta, \quad (A3)$$

where $\mathbf{T}_{\alpha a}$ is the Raman tensor and $Q_{\alpha a}$ is the lattice coordinate for the a th vibration of irreducible representation Γ_α . σ is proportional to the average value of $|\mathbf{P}|^2$.

$$\begin{aligned} \langle |\mathbf{P}|^2 \rangle &= \sum_{\alpha\alpha'} (\mathbf{T}_{\alpha\alpha} \cdot \hat{e}_\eta)^* \cdot (\mathbf{T}_{\alpha'\alpha'} \cdot \hat{e}_\eta) \langle Q_{\alpha\alpha} Q_{\alpha'\alpha'} \rangle \\ &= \sum_{\alpha\alpha'} \hat{e}_\eta \cdot (\mathbf{T}_{\alpha\alpha} \dagger \mathbf{T}_{\alpha'\alpha'}) \cdot \hat{e}_\eta \langle Q_{\alpha\alpha} Q_{\alpha'\alpha'} \rangle \\ &= \hat{e}_\eta \cdot \left(\sum_a \mathbf{T}_{\alpha a} \dagger \mathbf{T}_{\alpha a} \right) \cdot \hat{e}_\eta \langle Q_\alpha^2 \rangle, \end{aligned} \quad (A4)$$

since

$$\langle Q_{\alpha a} Q_{\alpha' a'} \rangle = \langle Q_\alpha^2 \rangle \delta_{\alpha a'}.$$

The product $\sum_a \mathbf{T}_{\alpha a} \dagger \mathbf{T}_{\alpha a}$ is a unit tensor. This can be seen by multiplication of the Raman tensors listed by Loudon²¹ (see also Fig. 2). Thus,

$$\langle |\mathbf{P}|^2 \rangle = \text{constant} \times \langle Q_\alpha^2 \rangle, \quad (A5)$$

independent of η . Therefore σ is independent of η . In Sec. III, we evaluate σ using

$$\sigma = \frac{8\pi}{3} \sum_k \left(\frac{d\sigma}{d\Omega} \right)_{kx}. \quad (A6)$$