Raman Effect in the F Center

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(Received 14 November 1963)

A discussion is given of the theory of the Raman effect in the F center. It is shown that the study of this effect could give new information about the F center that might lead to an understanding of its long radiative lifetime.

I. INTRODUCTION

THE F center in the alkali-halide crystals has been understood[1,2] rather completely for over twenty years. It was proposed by de Boer[3] and now generally accepted that the F center consists of an electron trapped at a halogen-ion vacancy. The electronic states of this system have recently been discussed by Gourary and Adrian.[4] The F absorption band in KCl, which may be considered typical, is centered[5] at 2.30 eV at 0°K and shifts to lower energy with increasing temperature, reaching 2.21 eV at 300°K. The width[5] (full width at half-maximum) increases from 0.36 eV at 0°K to 0.78 eV at 300°K. From the integrated absorption Dexter[6] finds that the oscillator strength (KCl) is 0.55. It was suggested by Gurney and Mott,[7] and later by Huang and Rhys,[8] that the F center should be a very efficient luminescence center at low temperatures. Nevertheless, Klick[9] failed to observe any luminescence which he could definitely attribute to the F center, and concluded that the radiative efficiency must be less than 3% in his samples. Botden, van Doorn, and Haven[10] observed a luminescence which they tentatively attributed to the F center, and estimated the radiative efficiency to be $\sim 1\%$. Subsequently a possible mechanism for the nonradiative decay of the excited state has been proposed by Dexter, Klick, and Russell.[11]

Recently the lifetime of the excited state has been measured directly by Swank and Brown.[12] These investigators observed both the luminescence and the photoconductivity excited by a short pulse of radiation in the F-absorption band. They showed that their results are in good agreement with a model which considers only two states, the ground state and an excited state which can decay to the ground state or be thermally ionized into the conduction band. The decay to the ground state, which they call the radiative decay, is assumed independent of temperature, while the ionization rate is assumed to be temperature-dependent with an activation energy ΔE. They find from their analysis $\Delta E \sim 0.15$ eV for KCl. Their most surprising result is that the lifetime of the excited state at low temperatures $T < 75$°K is found to be $\tau \sim 6\times 10^{-7}$ sec. This represents an upper limit to the radiative lifetime since it corresponds to a radiative efficiency at low temperatures of 100%; if the radiative efficiency is less than 100%, the true radiative lifetime is even longer. The lifetime observed is surprisingly long in view of previous estimates ranging from[2] 2×10^{-8} to[13] 6×10^{-9} sec. Fowler and Dexter[14] have carefully reconsidered the relation between emission and absorption processes in solids and now find a radiative lifetime for the F center in KCl of 5×10^{-8} sec. All of these estimates are based upon the assumption that the electric dipole-matrix elements are the same for emission and absorption. If these matrix elements (squared) differed by a factor of approximately 12, the observed lifetime could be explained. We shall refer to this factor as the *absorption-emission discrepancy*. Fowler and Dexter[14] have argued qualitatively that it is not unreasonable that the absorption-emission discrepancy may be as large as 12 in view of the Jahn-Teller distortion of the lattice that is undoubtedly associated with the degenerate ($2p$) excited state.

On the other hand, there may be no discrepancy at all. The explanation preferred by Swank and Brown[12] is that emission occurs from a metastable state below the ($2p$) state. Recently Wood[15] has shown that such a state slightly above the ($2p$) state may explain the K band. The oscillator strength is borrowed from the F band through interaction with vibrations, perhaps explaining the temperature dependence[12] of the F-luminescence lifetime at low temperatures. Wood does not believe,

[1] F. Seitz, Rev. Mod. Phys. **26**, 7 (1954); **18**, 384 (1946).
[2] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940).
[3] J. H. de Boer, Rec. Trav. Chim. **56**, 301 (1937).
[4] B. S. Gurary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10; see also Max Wagner, Z. Naturforsh. **15**, 889 (1960).
[5] G. A. Russell and C. C. Klick, Phys. Rev. **101**, 1473 (1956). A more recent configuration coordinate analysis based on careful measurements of the emission line shape of the F center has been given by F. Lüty and W. Gebhart, Z. Physik **169**, 475 (1962).
[6] D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6.
[7] R. W. Gurney and N. F. Mott, Proc. Phys. Soc. (London) **A49**, 32 (1937).
[8] K. Huang and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1950).
[9] C. C. Klick, Phys. Rev. **94**, 1541 (1954).
[10] Th. P. J. Botden, C. Z. van Doorn, and Y. Haven, Philips Res. Rept. **9**, 469 (1954). For more recent results see H. Pick, Nuovo Cimento Suppl. **7**, 498 (1958).
[11] D. Dexter, C. Klick, and G. Russell, Phys. Rev. **100**, 603 (1955).
[12] R. K. Swank and F. C. Brown, Phys. Rev. **130**, 34 (1963); Phys. Rev. Letters **8**, 10 (1962).
[13] J. J. Markham, Bull. Am. Phys. Soc. **7**, 197 (1962).
[14] W. B. Fowler and D. L. Dexter, Phys. Rev. **128**, 2154 (1962); Phys. Stat. Sol. **2**, 821 (1962); **3**, 1865 (1963).
[15] R. F. Wood, Phys. Rev. Letters **11**, 202 (1963).

however, that the metastable state is a likely explanation for the long lifetime. On the other hand, indirect support for the idea of Swank and Brown comes from the work of Mahr[16] on the bound excitons in KCl crystals containing I^- ions. He has found strong evidence that the absorption and emission involve different excited states, and suggests that the same may be true in the F center.

The question as to the role of metastable states and as to whether or not an absorption-emission discrepancy exists in the F center is therefore still open. In view of this, we propose that new information on the F center could be obtained by studying its *Raman effect.* It will be shown that the first-order Raman scattering is a direct measure of the absorption-emission discrepancy. Furthermore, the Raman effect appears to be the only method of observing directly the vibrations associated with the F center. From the temperature dependence of the width of the F-absorption band Russell and Klick[5] have concluded that the dominant vibration is a local mode of frequency (KCl) 2.6×10^{12} cps. On this basis they have set up a configuration coordinate description which accounts reasonably well for the Stokes shift and temperature dependence of the emission and absorption bands. Lax[17] has emphasized, however, that the configuration coordinate does not necessarily have significance as the coordinate of a normal mode of vibration. McCombie, Matthew, and Murray[18] have pointed out that a local mode should have a much higher frequency. They suggest that the F center interacts with the continuum (nonlocal) modes modified by the center so as to enhance the interaction with low-frequency modes. On this picture the spectrum of Raman frequency shifts would be broad and continuous, whereas on the local-mode picture it would be relatively sharply peaked at 2.6×10^{12} cps. The theory of the Raman effect is essentially the same for either picture, but the discussion here will assume a local mode to avoid introducing a lot of nonessential detail.

II. THEORY

The absorption-emission discrepancy may be measured by β in the relation

$$(\psi_{G1}|\mathbf{M}_{GF}(X)^2|\psi_{G1})=\beta^2(\psi_{F1}|\mathbf{M}_{GF}(X)^2|\psi_{F1}), \quad (1)$$

where ψ_{G1}, ψ_{F1} represent the lowest *vibrational* states associated with the ground *electronic* state "G" and excited electronic state "F" respectively, $\mathbf{M}_{GF}(X)$ is the matrix element of the dipole-moment operator between electronic states G and F, and X represents the positions of the ions. Figure 1 shows a configuration coordinate diagram for the F center in KBr after Russell and Klick.[5] The parabolas represent the potential energy of the lattice in the gound (G) and excited (F) electronic states as a function of a coordinate X representing the radial vibration of the six neighboring K^+ ions. On the right the vibrational levels are indicated with the spacing somewhat exaggerated for pictorial purposes.

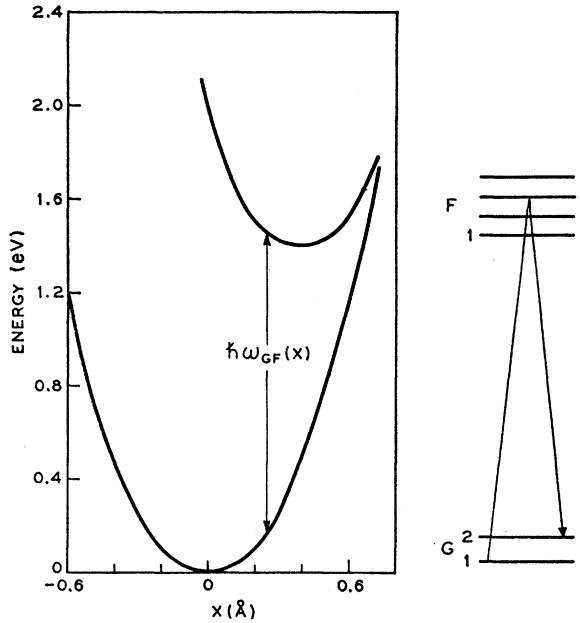

FIG. 1. Configuration-coordinate diagram for the F center in KBr showing the potential energy of the lattice as a function of a single coordinate X representing a radial vibration of the neighboring ions. The vibrational levels are indicated schematically on the right (spacing exaggerated) to show a Raman process.

It has been customary[18] in configuration coordinate analyses to neglect the dependence of $\mathbf{M}_{GF}(X)$ on X. This is not consistent with (1), so we express $\mathbf{M}_{GF}(X)$ as a linear function $\mathbf{M}_0+(X-X_G)\mathbf{M}'$, which it is convenient to write in the form

$$\mathbf{M}_{GF}(X)=(X-X_0)\mathbf{M}', \quad (2)$$

with $-X_0\mathbf{M}'=\mathbf{M}_0-X_G\mathbf{M}'$. In order to make use of the results of Russell and Klick[5] we must assume that X is a single coordinate (the configuration coordinate) referring to a fully symmetric local mode of vibration in which the six neighboring K^+ ions move radially toward and away from the Cl^- ion vacancy. This vibration will have different equilibrium positions in the electronic states G and F. If we denote the equilibrium positions by X_G, X_F, (1) can be rewritten approximately

$$\mathbf{M}_{GF}(X_G)=\pm\beta\mathbf{M}_{GF}(X_F). \quad (3)$$

From (2) and (3) X_0 can be determined:

$$X_0=(X_G\mp\beta X_F)/(1\mp\beta), \quad (4)$$

except for the ambiguity in the sign of β. In any case, if $|\beta|$ is large X_0 lies close to X_F. Since the oscillator strength f of the absorption band is known, we have

[16] H. Mahr, Phys. Rev. **130**, 2257 (1963).
[17] M. Lax, J. Chem. Phys. **20**, 1752 (1952).
[18] C. W. McCombie, J. A. D. Matthew, and A. M. Murray, J. Appl. Phys. Suppl. **33**, 359 (1962).

another relation:

$$\mathbf{M}'^2(X_G-X_0)^2=3f(\hbar e^2/2m\omega_{GF}), \tag{5}$$

where ω_{GF} is the angular frequency in absorption $(X=X_G)$.

We now consider the Raman scattering of the F center. The total power scattered at frequency ω is given formally[19,20] by

$$\begin{aligned} P_\omega&=\sigma_R I_0,\\ \sigma_R&=(8\pi/3)(\omega/c)^4(\alpha_R\cdot\mathbf{u}_0)^2,\\ \alpha_R&=\frac{1}{\hbar}\sum_\tau\left\{\frac{\mathbf{M}_{G1,\tau}M_{\tau,G2}}{\omega_{G1,\tau}-\omega}+\frac{\mathbf{M}_{\tau,G2}\mathbf{M}_{G1,\tau}}{\omega_{G1,\tau}+\omega_0}\right\}, \end{aligned} \tag{6}$$

where I_0 is the intensity *in the medium* of the incident wave, σ_R is the total Raman cross section, α_R is called the Raman polarizability tensor, $\mathbf{u}_0$ is the unit polarization vector of the incident wave, G_1 and G_2 denote the first two vibrational states associated with electronic state G, and τ denotes any electronic-vibrational intermediate state. Figure 1 shows a typical process in which τ is the state $F3$. The radiated power P_ω is just the total radiation from a classical dipole moment $\mathbf{M}=\alpha_R\mathbf{E}_0$, where $\mathbf{E}_0$ is the amplitude of the incident wave. The refractive index of the medium cancels out of (6). The scattered frequency is $\omega=\omega_0-\omega_G$, where ω_G is the vibration frequency in electronic state G, and ω_0 is the incident frequency.

In the Born-Oppenheimer approximation[6] the electronic-vibrational states have the form

$$|G1\rangle=\Phi_G(x,X)\psi_{G1}(X), \tag{7}$$

where x represents the electron coordinates. We assume that $|\omega_{G1,\tau}-\omega|$ in (6) is much larger than the vibrational frequency ω_τ in state τ. Then the vibrational states of state τ can be summed immediately and we can regard τ as denoting just an electronic state $\Phi_\tau(x,X)$. The polarizability can then be written as a matrix element between vibrational states

$$\begin{aligned} \alpha_R&=(\psi_{G1}|\alpha(X)|\psi_{G2}),\\ \alpha(X)&=\frac{1}{\hbar}\sum_\tau\left\{\frac{\mathbf{M}_{G\tau}\mathbf{M}_{\tau G}}{\omega_{G\tau}-\omega_0}+\frac{\mathbf{M}_{\tau G}\mathbf{M}_{G\tau}}{\omega_{G\tau}+\omega_0}\right\},\\ \mathbf{M}_{G\tau}(X)&=\int dx\Phi_G^*(x,X)\mathbf{M}\Phi_\tau(x,X). \end{aligned} \tag{8}$$

In view of the large oscillator strength of the F-absorption band, it is sufficient to consider only the single intermediate state $\tau=F$. Furthermore, $\alpha(X)$ must reduce to a scalar because of the cubic symmetry of the F center and the vibration we have assumed. Thus, we denote by M any Cartesian component of the dipole-moment operator and write

$$\alpha(X)=\frac{1}{\hbar}\frac{2\omega_{GF}}{\omega_{GF}^2-\omega_0^2}M_{GF}(X)^2, \tag{9}$$

where we have assumed for convenience that $M_{GF}(X)$ is real. From (2), (5), and (8)

$$\begin{aligned} \alpha_R&=\frac{1}{\hbar}\frac{2\omega_{GF}}{\omega_{GF}^2-\omega_0^2}\left(\frac{\mathbf{M}'^2}{3}\right)(\psi_{G1}|(X-X_0)^2|\psi_{G2})\\ &=f\frac{e^2}{m(\omega_{GF}^2-\omega_0^2)}\frac{(\psi_{G1}|(X-X_0)^2|\psi_{G2})}{(X_G-X_0)^2}. \end{aligned} \tag{10}$$

We now assume that the amplitude of vibration is small compared to $|X_G-X_F|$ and to $|X_G-X_0|$; then we can write

$$(\psi_{G1}|(X-X_0)^2|\psi_{G2})=2(X_G-X_0)(\hbar/2M\omega_G)^{1/2}, \tag{11}$$

where M is a suitable reduced mass for the vibration and ω_G is the vibration frequency. Finally we can eliminate X_0 from (4) and obtain

$$\alpha_R=f\frac{e^2}{m(\omega_{GF}^2-\omega_0^2)}\left(\frac{\beta-1}{\beta}\right)\left[\frac{2\hbar/M\omega_G}{(X_G-X_F)^2}\right]^{1/2}, \tag{12}$$

where β may have either sign. This relation shows how the Raman scattering is a measure of the absorption-emission discrepancy. For $\beta=+1$ (no discrepancy) the Raman scattering of the F center would vanish; this is the case corresponding to the usual assumption that M_{GF} is independent of X (the Condon approximation).[17]

The last factor in (12) is a measure of the ratio of the vibration amplitude to the displacement of the equilibirum position of the vibration between states G and F. We can estimate it from the analysis of Russell and Klick[5] who find $|X_G-X_F|\sim4\times10^{-9}$ cm, $\omega_G/2\pi=2.6\times10^{12}$ sec, and $M(6\text{K}^+\text{ ions})=3.7\times10^{-22}$ g; thus

$$(2\hbar/M\omega_G)^{1/2}/(X_G-X_F)\sim0.14, \tag{13}$$

which justifies the assumption in (11) that the vibration amplitude is small. Our numerical result, therefore, is for the *polarizability*

$$\alpha_R=(1.3\times10^{-24})\left(\frac{\beta-1}{\beta}\right)\left(1-\frac{\omega_0^2}{\omega_{GF}^2}\right)^{-1}\text{cm}^3, \tag{14}$$

and for the *cross section*

$$\sigma_R=3\times10^{-27}\left(\frac{\beta-1}{\beta}\right)^2\frac{(\omega_0/\omega_{GF})^4}{[1-(\omega_0/\omega_{GF})^2]^2}\text{cm}^2. \tag{15}$$

III. DISCUSSION

The usual situation in Raman spectroscopy is that $\hbar\omega_0$ is small compared to the energy of the strong elec-

[19] San-Ichiro Mizushima, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 26.

[20] J. Brandmüller and H. Moser, *Einführung in die Ramanspektroskopie* (Dr. Dietrich Steinkopff Verlag, Darmstadt, 1962). For a discussion of Raman intensity measurements see Sec. 113.

tronic transitions in the material. In (14) this would mean $\omega_0^2 \ll \omega_{GF}^2$. Under these conditions α_R is independent of ω_0 while σ_R varies as ω_0^4, making α_R more convenient than σ_R for describing the strength of the Raman effect. Raman strengths have been measured[20] for a number of molecules by comparing the intensities of the Raman and Rayleigh scattering. This measures α_R^2/α^2, where α is the ordinary polarizability which can be related to the contribution of the molecule to the refractive index. In this way, it has been found that in typical strong Raman lines α_R is of the order[20]

$$\alpha_R \sim 2\times 10^{-25}\ \text{cm}^3\ (\text{liquid } CCl_4), \tag{16}$$

while (14) gives for $\beta = +12^{1/2} = 3.5$

$$\alpha_R \sim 9\times 10^{-25}\ \text{cm}^3\ (F\ \text{center}). \tag{17}$$

This value would apply for incident light in the red or infrared ($\hbar\omega_0 < 2.3$ eV); for example the He–Ne laser ($\lambda = 11526$ Å, $\hbar\omega_0 = 1.07$ eV) might be used as the light source. Thus, we expect the F center to have a somewhat stronger Raman effect in the red than typical molecules if the absorption-emission discrepancy exists.

The theory of the preceding section, of course, does not apply if ω_0 is very close to ω_{GF}, the *resonance case.* This case is often very important in practice because the Raman scattering is larger, and additional information may be obtained since α_R is not required to be a symmetric tensor in this case. In the case of the F center, however, it does not apppear that the resonance case is likely to be very important because of the great breadth of the F-absorption band. A simple consideration shows that α_R for the resonance case $\omega_0 = \omega_{GF}$ is obtained by multiplying (17) by the factor $(\omega_{GF}/\Delta\omega) \sim 6$; thus there is only a modest enhancement over the ordinary Raman effect. There may actually be a great reduction of the measured scattering due to the strong absorption of both the incident and scattered waves in the sample. Whether there is any advantage to operating in the F-absorption band will depend on the concentration of F centers.

Due to the relatively low energy of the F-absorption band (2.3 eV) compared to the intrinsic absorption of the alkali-halide crystals (7.4 eV in KCl) it is possible to operate in the range $\omega_0^2 \gg \omega_{GF}^2$. This is a rather unique property of the kind of system we are considering, since usually a material becomes opaque at all energies above the strong electronic transitions. In the high-energy region α_R goes as ω_0^{-2} while σ_R becomes constant. Thus, σ_R now becomes more convenient than α_R for describing the Raman strength. For $\beta = +12^{1/2}$ the cross section becomes

$$\sigma_R \sim 1\times 10^{-27}\ \text{cm}^2\ (F\ \text{center}). \tag{18}$$

This would apply, for example, if the incident wave were from a Hg source producing the 2536 Å resonance line (4.9 eV). The greater ease of observing the Raman scattering at high energies may be surmised by comparing (18) with the cross section (6×10^{-30} cm^2) recently reported[21] for nitrobenzene at the ruby-laser energy (1.8 eV). It follows that in the high-energy region the total Raman scattering of the F center represents an easily detectable power (unless $\beta = +1$).

Whether the Raman scattering can actually be observed will depend not only on σ_R but also on the line shape. If the vibrational mode is too broad nothing will be seen. Here, however, one has the great advantage in this system that the Raman scattering by the perfect crystal lattice is forbidden in first order. Thus, the background should be quite low permitting a very broad Raman spectrum to be seen.

One might consider whether other optical centers in solids should also be studied in Raman effect. The greatest interest is in centers that have been extensively analyzed by configuration-coordinate methods. Besides the F center the most conspicuous example is the Tl^+ center in KCl which has been analyzed by Williams[22] and Knox and Dexter.[23] This center is somewhat less favorable than the F center because of its relatively high (6 eV) absorption energy. All centers in crystals of the diamond, zincblende, or wurzite type are considerably less favorable because the vibrations of the perfect lattice are Raman active. It might also be pointed out that the phonon structures of the sharp exciton lines in many of these crystals are clearly seen in the luminescence spectra, and appear to be due in all cases to phonons of the perfect crystal (i.e., not local modes).[24] There is therefore less to be learned from a Raman study of such centers. We conclude that the F center holds the greatest promise of yielding interesting information from a Raman investigation.[25]

[21] R. W. Hellwarth, Appl. Opt. **2**, 847 (1963).
[22] F. E. Williams, J. Chem. Phys. **19**, 457 (1951).
[23] R. S. Knox and D. L. Dexter, Phys. Rev. **104**, 1245 (1956).
[24] Consider, for example, the case of GaP described by D. G. Thomas, M. Gershenzon, and J. J. Hopfield, Phys. Rev. **131**, 2397 (1963).
[25] R. J. Elliot and R. Loudon, Phys. Letters **3**, 189 (1963), have proposed that studies should be made of the electronic Raman effect in transition and rare-earth-impurity ions. The mechanism of this effect differs from that considered here, which is the usual vibrational Raman effect. Experimentally, both effects would be studied in the same way, and careful interpretation would be required to distinguish them. In the case of the F center this should present no difficulty.