RAMAN SCATTERING BY *F* CENTERS

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F centers in alkali-halide crystals possess strong broad absorption and fluorescence bands in the near ultraviolet, visible, and near infrared. The breadth of these bands is characteristic of electronic transitions in the alkali halides, and is indicative of strong coupling between electrons and phonons. Much effort has been devoted to the understanding of this coupling and, in particular, of the quantitative band breadth, band shape, and energy shift between absorption and fluorescence bands for *F* centers.[1] Information about the interaction of *F* centers with lattice vibrations is contained also in their infrared and Raman spectra. The infrared spectrum of *F* centers has not yet been observed, probably because it coincides with the strong intrinsic (Reststrahl) spectrum. We report here the first observations of Raman scattering from *F* centers, which provide the first direct information about the vibrational interactions of *F* centers.

This work was stimulated by the suggestion of Kleinman[2] that the unexpectedly long radiative lifetime of the *F* center[3] might imply a large Raman cross section. This possibility, and the ability to achieve near resonance between the optical transition of the *F* center and the exciting light, led us to believe that the experiments were feasible, in spite of the extreme diluteness of the scattering centers.

We have produced nitrogen-temperature Raman spectra from single crystals of KCl and NaCl colored both additively and by γ radiation from a cobalt source. The narrow-band, polarized exciting radiation was obtained from helium-neon (6328Å) and argon ion (5145 and 4880Å) lasers. The light was chopped and the Raman spectrum measured photoelectrically by synchronous phase-sensitive detection.[4] The spectrometer used was a tandem $\frac{3}{4}$-m Czerny Turner grating spectrometer manufactured by Spex Industries, Inc. This instrument provided good isolation of the unshifted scattered light and freedom from grating ghosts, and was operated with a spectral resolution of about 10 Å.

In these experiments, the incident light, in a narrow beam, passed vertically through the crystal, and the direction of observation was horizontal and perpendicular to the polarization of the beam. The narrow linear source of scattered radiation was focused onto the entrance slit of the spectrometer, and polarization of the Raman radiation was observed simply by inserting a polarizer in front of the entrance slit.

Figure 1 shows nitrogen-temperature absorption curves for *F* centers in KCl and NaCl and the positions of the exciting lines. Raman spectra were taken also at nitrogen temperature, for two reasons: (1) to narrow the *F* bands sufficiently to allow the laser line to be close to, but not too deep into, the absorption bands, and (2) to stabilize the *F* centers against bleaching and coagulation.

In Figs. 2(a)-(d) we show the Raman spectrum of a crystal of NaCl colored in the gamma cell at room temperature for 16 hours and possess-

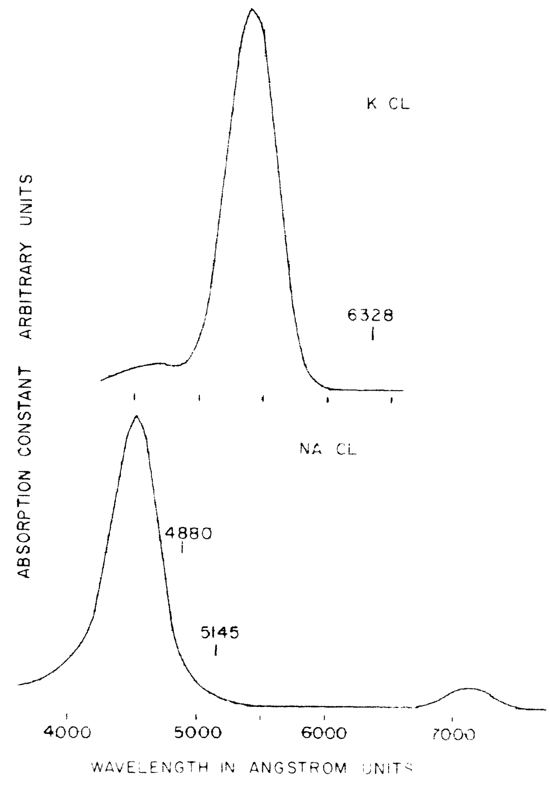

FIG. 1. Absorption bands for *F* centers in KCl and NaCl, measured at liquid-nitrogen temperature. Positions of laser emission lines are also shown.

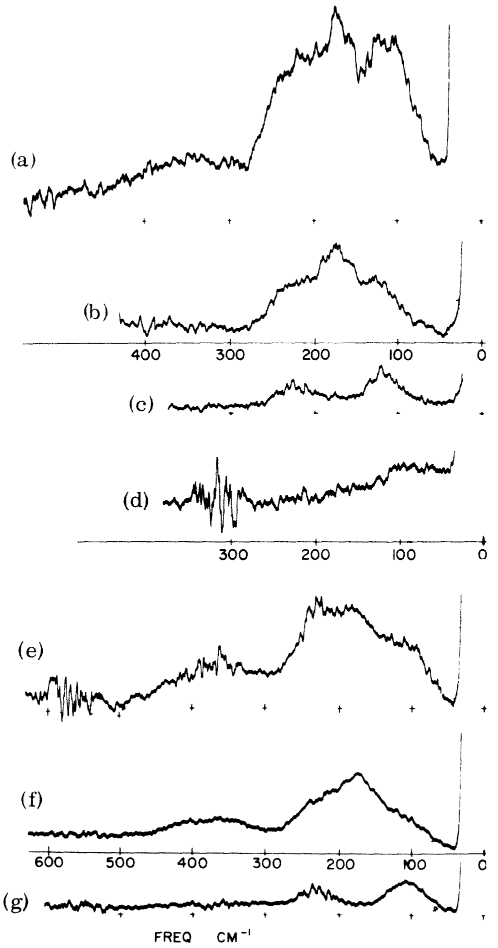

FIG. 2. Raman effect of F center in NaCl: (a) unpolarized spectrum; (b) polarized parallel to laser light; (c) polarized perpendicular to laser light [(a)-(c) on Stokes side]; (d) unpolarized anti-Stokes scattering [(a)-(d) with 5145Å line of argon ion laser]; (e) unpolarized spectrum, (f) polarized parallel to laser light, (g) polarized perpendicular to laser light [(e)-(g) with 4880Å line of argon ion laser].

ing 10^{17} F centers/cc. The exciting light was the 5145Å line of the argon ion laser. This spectrum divides nicely into two polarized bands, centered at 175 and 350 cm^{-1}, and two depolarized bands, at 115 and 235 cm^{-1}.

Figures 2(e)-(g) show the Raman spectrum of the same NaCl sample, taken with the 4880Å line of the argon ion laser. The spectrum is slightly distorted by the changing absorption in the shoulder of the F band, and no anti-Stokes measurements were possible. All the features of the spectrum in Figs. 2(a)-(c) are repeated here, providing proof that the phenomenon we are observing is, in fact, Raman scattering, and not some new kind of fluorescence.

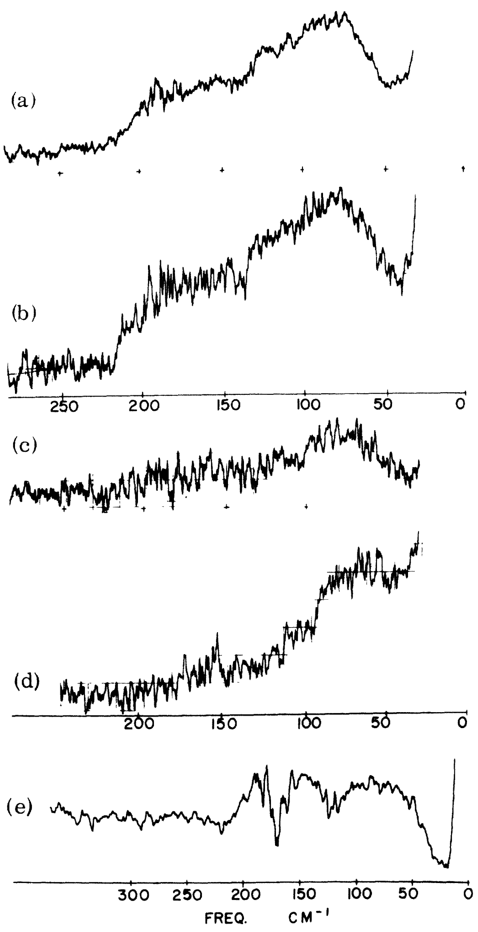

FIG. 3. Raman effect of F center in KCl: (a) unpolarized spectrum, (b) polarized parallel to laser light, (c) polarized perpendicular to laser light [(a)-(c) on Stokes side]; (d) unpolarized anti-Stokes scattering [(a)-(d) additively colored sample]; (e) unpolarized spectrum of irradiated sample. All spectra taken with 6328Å line of the He-Ne laser.

Figures 3(a)-(d) show the Raman spectrum of a crystal of KCl colored additively with approximately 6×10^{17} F centers/cm^3. On the Stokes side there appears a broad double band with little in the way of reliably resolvable structure, extending from about 40 to 200 cm^{-1}, with its maximum near 80 cm^{-1}. This radiation is almost entirely polarized. On the anti-Stokes side, the radiation is much weaker, and concentrated in a region of much smaller energy shift, because of the low temperature (78°K corresponds to 54 cm^{-1}). In fact, in the Stokes radiation, nearly one-third of the peak at 80 cm^{-1} is stimulated by the presence of thermal phonons, while the other two-thirds is spontaneous, and will remain at lower temperatures. Although it is not shown here, the anti-Stokes Raman radiation is also almost completely polarized.

The different parts of Fig. 3 are not directly comparable because of changes in the electronic gain.

Figure 3(e) shows the unpolarized Raman spectrum of a crystal of KCl colored by cobalt gamma rays for 16 hours at room temperature in a source of strength 5×10^5 R per hour. The same characteristic features are apparent. The noisy dip in the trace at about 180 cm^{-1} arises because of fluorescent emission at 6400 Å in the laser. The F-center density was approximately 6×10^{16} per cm^3.

The most important conclusion to be drawn from these observations is that there is no evidence for a strong sharp localized mode of vibration. Measurements at higher spectral resolution have shown no sharpening of the features of the spectra.

The interpretation of the Raman spectra must therefore involve the intrinsic phonon spectra, and as a result will provide new knowledge about phonons. From this point of view, the main role of the center is to destroy conservation of wave vector and allow first- and higher-order Raman scattering by phonons more or less throughout the Brillouin zone. Information obtained in this way can be used to supplement that from infrared and Raman studies on pure crystals, where wave vector is conserved, and where virtually all processes are second order. In addition, one can expect to learn something new about F centers from their preference for interaction with certain phonons and not with others.

We propose the following analysis of the F-center Raman spectrum in NaCl based on the calculated dispersion curves of Hardy and Karo.[5] The low-energy depolarized band corresponds to transverse acoustic phonons near point L in the Brillouin zone (112 cm^{-1}). The large complex polarized band is a composite of longitudinal acoustic at Δ (150 cm^{-1}), longitudinal acoustic at L (160 cm^{-1}), longitudinal optic at Δ (about 190 cm^{-1}: no true maximum in density of states), and longitudinal optic at Λ (about 240 cm^{-1}: no true maximum). The depolarized band at 235 cm^{-1} and the broad polarized band at 350 cm^{-1} are second order Raman peaks and correspond to similar features in the intrinsic Raman spectrum measured by Welsh, Crawford, and Staple[6] and interpreted by Burstein, Johnson, and Loudon[7] as second-order processes at points X, L, and Δ.

Analysis of the KCl Raman spectrum has not been successful, primarily because of difficulty in assigning the polarized band below 100 cm^{-1}. This may be an indication of the existence of a rather broad quasilocalized mode at 80 to 90 cm^{-1}. This would be consistent with Russell and Klick's value of 90 cm^{-1} for the frequency of a single-configuration coordinate oscillator responsible for the broadening of the F band.[8]

We are attempting to obtain better resolution of singularities in the Raman spectra, by increasing the signal-to-noise ratio and by cooling the sample to liquid-helium temperature.

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[1] For a review of the various models used for calculating properties of F centers, see J. H. Schulman and W. D. Compton, Color Centers in Solids (Pergamon Press, New York, 1962), Section 3.5.

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