IV. CONCLUSION

Equation (14) indicates that the intensity of the vibronic line increases as the fifth power of its displacement from the no-phonon line (i.e., as the fifth power of absorbed-phonon frequency) in the rocksalt lattice. Equation (15), however, indicates that the absence of a center of symmetry about the transition ion in the zinc blende structure results in an intensity proportional to the third power of the absorbed-phonon frequency. If the diagonal vibronic terms of Eq. (8′) were dominant over the nondiagonal term it can be easily seen that the intensity would be proportional to the first power of the absorbed phonon frequency. Since high powers of the sound velocities appear in the denominators of both transition rates we conclude that the lower velocity transverse phonons dominate over the longitudinal phonons. It should be emphasized that these conclusions refer only to the long-wavelength "tail" of the vibronic line where the Debye approximation and the strain analysis can be reasonably expected to hold.

The frequency dependence found in Eq. (14) has also been derived independently by Schawlow[1] and by Loudon.[2]

ACKNOWLEDGMENTS

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[1] A. L. Schawlow (private communication).

[2] Quoted by M. V. Hobden, Phys. Letters **15**, 10 (1965).

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Vibronic Transitions in Ruby and MgO:V^{2+}†

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Experiments are described on the low-temperature optical fluorescence of Al$_2$O$_3$:Cr^{3+} and MgO:$^{2+}$, in which the vibronic side-band intensity near the sharp *R* line is measured as a function of the energy separation $\hbar\omega$ from the no-phonon *R* line. The results are in reasonable agreement with Vredevoe's theory, which predicts for low ω an intensity proportional to ω^3 for Al$_2$O:Cr^{3+}, and to ω^5 for MgO:V^{2+}.

INTRODUCTION

At low temperatures the sharp-line optical fluorescence spectrum of an impurity ion in a crystal consists primarily of purely electronic transitions, in which a photon is emitted and the impurity ion makes a transition from a higher to a lower electronic state. Associated with these purely electronic transitions are vibronic transitions, in which both a photon and a phonon are emitted, with the sum of their energies being equal to the electronic energy difference. A simple classical picture implies that the purely electronic transition is modulated by the lattice vibrations, and that the resulting side bands give rise to the observed vibronic transitions.

In general, the electronic transition may be either an electric or a magnetic dipole transition, and it is of interest to investigate the detailed nature of the vibronic side band for each case. Our experimental investigations concern two substances: ruby (Al$_2$O$_3$:Cr^{3+}), and MgO:V^{2+}. In both substances, the impurity ion has a configuration $3d^3$, and at 2°K, the $^2E \longrightarrow {}^4A_2$ (*R*-line) fluorescence spectrum consists of a single sharp line with its vibronic side band extending for several hundred cm^{-1} to the low-energy side of the sharp line (see Fig. 1). For ruby, the Cr^{3+} impurity is not at a center of inversion in the corundum lattice, and the *R* line is an electric dipole transition, while for MgO:V^{2+}, the ion does lie at a center of inversion, and the *R* line is a magnetic dipole transition. For each case, Vredevoe[1] has made theoretical predictions concerning the intensity of the vibronic side bands in the region close to the *R* line, i.e., in the limit $ka \ll 1$, where k is the magnitude of the phonon wave vector, and a is the lattice constant. He finds that in both cases, the side bands are predominantly electric dipole; that in the case of a noncentrosymmetric ion (ruby), the intensity I_s of the vibronic side band is proportional to the third power of the phonon frequency ω, while for a centrosymmetric ion (MgO:V^{2+}), I_s is proportional to the fifth power of the phonon frequency.[1a] It is interesting to note that for

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[1] L. A. Vredevoe, preceding paper, Phys. Rev. **147**, 541 (1966).

[1a] *Note added in proof.* If the no-phonon line is electric dipole (e.g. ruby) it is also possible for a term linearly proportional to ω to be present in the sideband intensity. [M.V. Hobden, Phys. Letters **15**, 10 (1965).] While it is possible that the intensity A observed here arises from such a term, our data are not well fitted by an equation of the form $a\omega + b\omega^3$. We are grateful to Dr. Rodney Loudon for correspondence on this point.

the latter case one may have an electric dipole side band even when the no-phonon R line occurs only as a magnetic dipole transition.[2] The reason for this is clear: The odd vibrational modes of the octahedral cluster surrounding the V^{2+} ion will destroy the inversion symmetry, thus allowing the vibronic transitions associated with such modes to occur as electric dipole transitions. As indicated by Vredevoe, the interaction of the ion with such odd vibrational modes may be expressed in terms containing the first derivatives of the strain, and this leads to the additional factor of ω^2 in the side-band intensity. This factor would not be present if the side band were magnetic dipole, and thus by measuring the frequency dependence of the side-band intensity, it is possible to determine whether the side band is electric or magnetic dipole.

EXPERIMENTS

Two ruby crystals are used in our experiments, one Linde ruby grown by the flame fusion (Verneuil) method, the other a flux-melt ruby grown by J. P. Remieka of Bell Telephone Laboratories. Both have chromium-ion concentrations of less than 0.005% in order to suppress lines caused by chromium-ion pairs. The crystals are immersed in superfluid helium at approximately 2°K, and the R_1 line fluorescence is excited using a 1-kW General Electric AH-6 mercury arc lamp whose light is filtered by a copper-sulfate solution. The fluorescent spectrum is observed using a $\frac{3}{4}$ meter Spex grating spectrometer in first order (dispersion $\approx$4.5 Å/mm) equipped with a cooled RCA 7102 photomultiplier tube.

For the experiments on MgO:V^{2+}, two crystals are also used, both supplied by the Norton Company, each having been heated in a hydrogen atmosphere[3] to stimulate the formation of V^{2+}. These crystals are also immersed in liquid helium, and the V^{2+} R-line fluorescence (in the region of 8700 Å) is excited using a 600 W Sylvania tungsten-iodine "Sun-Gun" lamp whose light is filtered by a container of water. The fluorescent spectrum is observed as described above for ruby. Several measurements are made for each of the four crystals, using different slit widths and different system

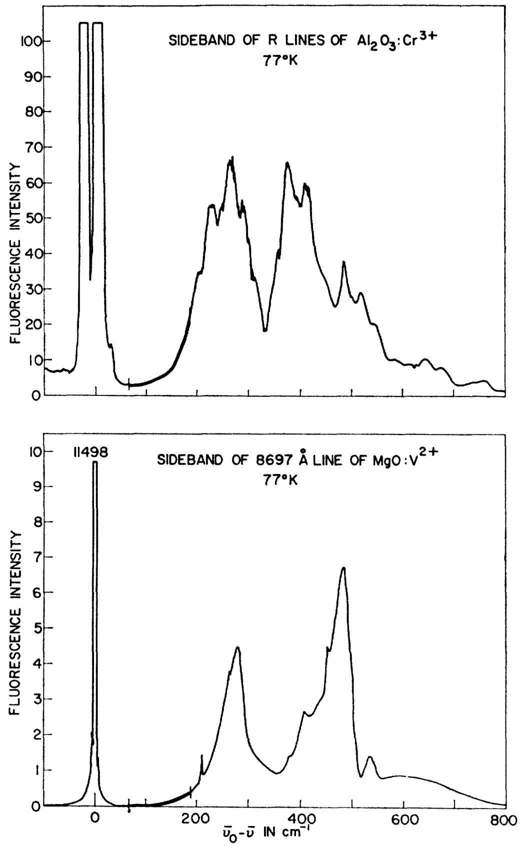

FIG. 1. The fluorescence spectrum in the region of the R lines for (a) Al_2O_3:Cr^{3+}, and (b) MgO:V^{2+}. In each figure, the approximate region studied is indicated by tick marks superposed on the side-band intensity trace. In (a), the R_2 line and its associated side band also appear; these are not present in the studies reported here, which are done at $T\approx 2$°K.

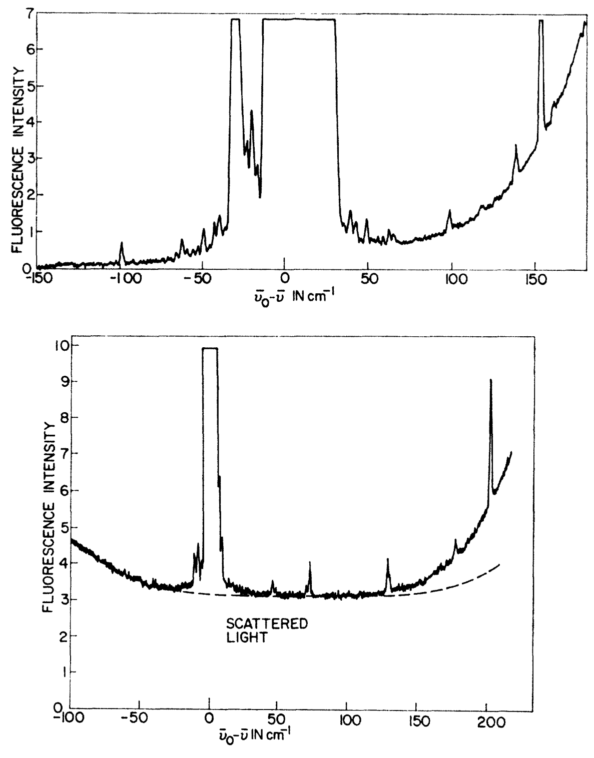

FIG. 2. Typical raw data showing the detailed fluorescence spectrum close to the R lines for (a) Al_2O:Cr^{3+} and (b) MgO:V^{2+}, showing the qualitative increase in the side-band intensity with increasing $\bar{\nu}_0-\bar{\nu}$ for each substance. In (a) many of the small lines seen are grating ghosts of the R line; in (b) the scattered light intensity is indicated by a dashed line.

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[2] Indications of the electric dipole nature of the R-line vibronic side band in MgO:V^{2+} are contained in the Ph.D. dissertation of G. F. Imbusch, Stanford University, 1964 (unpublished).

[3] M. D. Sturge, Phys. Rev. 130, 639 (1963).

gains; Fig. 2 illustrates representative traces for each type of crystal.

In the analysis of our data, the side-band intensities are corrected for the system response and for the source light scattered from the crystals. For the ruby crystals, the position of the baseline ($I_s=0$) is determined by assuming that the intensity of the no-phonon line is symmetric about the line center so that its intensity may thus be subtracted from the observed total intensity to the low-energy side of the no-phonon line. In this manner we obtain a log-log plot of I_s versus $(\bar{\nu}_0-\bar{\nu})$ as shown in Fig. 3. Here I_s is the measured side-band intensity in arbitrary units, and $(\bar{\nu}_0-\bar{\nu})$ is the separation from the no-phonon line in cm^{-1}. The phonon energy is given by $\hbar\omega=hc(\bar{\nu}_0-\bar{\nu})$. For most of our data, such a plot does not yield an entirely straight line, the data being best fitted by an equation of the form

$$I_s(\bar{\nu}_0-\bar{\nu})=A+B(\bar{\nu}_0-\bar{\nu})^n. \qquad (1)$$

For data in the frequency range shown in Fig. 3, the average value of n for ten runs is given by $n=3.2\pm0.2$ (Al_2O_3:Cr^{3+}). The small "extra" intensity A may perhaps arise from no-phonon lines which are shifted to the red by macroscopic crystal strains.

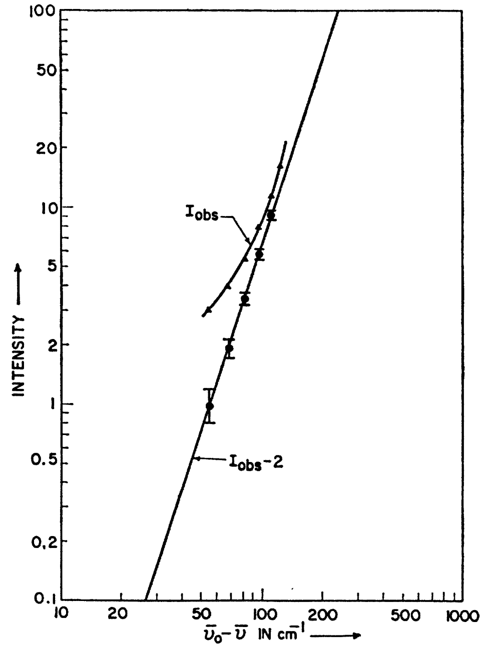

FIG. 3. A log-log plot of intensity versus $\bar{\nu}_0-\bar{\nu}$ for the ruby R-line side band. The upper curve is the observed intensity of the fluorescence; the lower curve is obtained by subtracting a constant intensity $A=2$ from the observed intensity [see Eq. (1)]. The slope of the straight line is ~2.7 for this measurement.

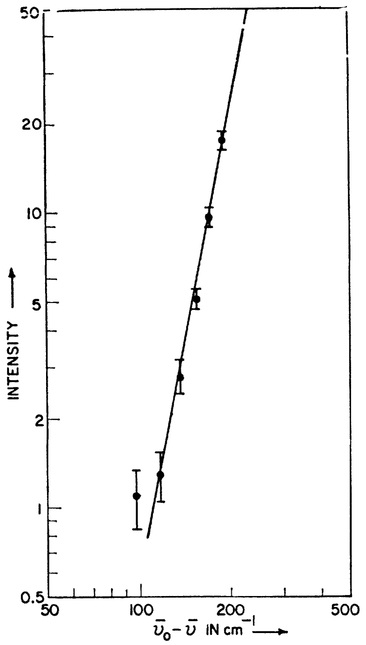

FIG. 4. A log-log plot observed intensity versus $\bar{\nu}_0-\bar{\nu}$ for the MgO:V^{2+} R-line side band. The slope of the straight line is ~5.1 for this measurement.

Similar data for a run on an MgO:V^{2+} crystal is shown in Fig. 4, which may be fit by an equation of the form

$$I_s(\bar{\nu}_0-\bar{\nu})=B(\bar{\nu}_0-\bar{\nu})^n, \qquad (2)$$

where the average value of n computed for eight runs is given by $n=5.4\pm0.5$ (MgO:V^{2+}).

If one examines the side-band intensity for higher phonon energies than those shown above, one finds that I_s increases more rapidly with ω than ω^3 (ruby) or ω^5 (MgO:V^{2+}). We expect such behavior as the long-phonon-wavelength restriction is violated and higher order terms become important.

CONCLUSIONS

For both Al_2O_3:Cr^{3+} and MgO:V^{2+}, our measurements appear to support Vredevoe's theory, which predicts $I_s\sim\omega^3$ for the former case, and $I_s\sim\omega^5$ for the latter. Our experiments also indicate that the vibronic side bands in both cases are electric dipole.

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