

entropic contribution when changes in the force constants are neglected at all. In a more realistic situation when both loss of coupling and elastic distortion are taken into account, it is not certain that the total self-entropy may be split into two terms which depend separately on these two kinds of perturbation. It then follows that our result cannot be added to the entropy change coming from the perturbation on the force constants only. From Table II, it appears that the present value is an order of magnitude higher than Huntington's previous estimate; this fact suggests that

the usual calculations, which neglect the influence of the loss of coupling might underestimate the actual entropy of a vacancy in monatomic lattices.

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### Temperature-Dependent Linewidth of Excited States in Crystals. I. Line Broadening due to Adiabatic Variation of the Local Fields\*

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The effect of strains on the linewidth of the optical spectra of paramagnetic ions in ionic crystals is briefly discussed and applied to the  ${}^2E$  state of ruby. A mechanism for the broadening of spectral lines in crystals at elevated temperatures is introduced. This mechanism assumes that the linewidth is due to "slow" variation in the local electric field of an individual ion. This theory should hold for states which do not interact with the crystal field to first order and is applied to the  ${}^2E$  states of ruby. The agreement between theory and experiment is quite good.

#### A. INTRODUCTION

IT is well known that the linewidth of absorption and emission lines in paramagnetic solids is generally much larger than the inverse of the natural lifetime of these lines. This condition holds even when zero temperature is approached ( $0^\circ\text{K}$ ). To be sure, the linewidth tends to decrease with temperature at fairly high temperatures; but below some temperature, generally in the range  $35\text{--}80^\circ\text{K}$ , the decrease stops.

Recently Schawlow<sup>1,2</sup> and others have given some compelling evidence for the  $R_1$  and  $R_2$  lines of  $\text{Cr}^{3+}$ , that the residual linewidth is chiefly due to strains in the crystal. Strains in chromium-doped  $\text{MgO}$  have been discussed rather thoroughly in reference 2 with the conclusion that the low-temperature linewidth may be due to this cause.

Due to strains, different ions are subjected to different local crystalline fields. By annealing ruby and  $\text{MgO}$  crystals doped with  $\text{Cr}^{3+}$  the linewidth has been decreased by an order of magnitude. (Annealing can remove only macroscopic strains; that is, where many neighboring ions have identical fields but ions in distant parts of the crystal "see" different fields.) It is not clear

whether the residual excess linewidth after annealing is due to remaining macroscopic strains, microscopic strains (differences in crystal field of neighboring  $\text{Cr}^{3+}$  ions) or other causes.

In the low-lying states of paramagnetic ions in crystals, the natural radiative linewidth is always negligible. However, nonradiative relaxations will often broaden lines when the states concerned interact directly with the lattice oscillators, and the energy separations are favorable. This broadening is the analog of spontaneous emission, with phonons replacing photons. As an example, it would be conceivable in ruby that the upper doublet of  ${}^2E$  (the  $R_2$  level, often designated  $2A$ ) could be broadened by direct relaxation to the  $R_1$  level ( $\bar{E}$ ). This would require the spontaneous emission of phonons at low temperatures. That this does not occur is due to the fact that no vibrations couple  $\bar{E}$  to  $2A$  in first order. The higher order relaxation of  $2A \rightarrow \bar{E}$  is discussed in reference 3.

In the rare earths, on the other hand, there are typically groups of closely spaced energy levels (the typical crystal field splitting of a Stark manifold  $\sim 10\text{--}200\text{ cm}^{-1}$ ) which are coupled directly by the crystal field. In such a case we expect direct relaxations within a Stark manifold to play a role in broadening of the lines. The  ${}^4T_2$  state of ruby is another example of

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<sup>1</sup> A. L. Schawlow, *J. Opt. Soc. Am.* **51**, 472 (1961).

<sup>2</sup> A. L. Schawlow, A. H. Piksis, and S. Sugano, *Phys. Rev.* **122**, 1469 (1961).

<sup>3</sup> J. Singer, *Quantum Electronics* (Columbia University Press, New York, 1961), Vol. II, (paper by A. Kiel).



where  $^4A_2$  is the ground state,  $^4T_2$  is the green band, and  $\zeta$  is the spin-orbit coupling parameter.

$$\delta D \cong \frac{4}{3} \frac{\delta K \times (250)^2}{(18\,000)^2} \cong 2.5 \times 10^{-4} \delta K.$$

If we use the value of  $\delta K = 0.5 \text{ cm}^{-1}$  necessary to explain the low-temperature linewidth of the  $^2E \rightarrow ^4A_2$  optical transition, we get

$$\delta D \cong 1.1 \times 10^{-4} \text{ cm}^{-1}.$$

For magnetic field along the  $c$  axis the linewidth of  $\pm \frac{1}{2} \rightarrow \pm \frac{3}{2}$  should be about  $2.2 \times 10^{-4} \text{ cm}^{-1}$  or 2.4 gauss.

The linewidth of the  $+\frac{1}{2} \rightarrow -\frac{1}{2}$  transition should be about a factor of 10 smaller since this broadening is due to variation in  $g$  (which results from a variation in  $10 Dq$ , the cubic-field parameter).

The strain linewidth of the ground state is therefore smaller than the broadening caused by the nuclear spin of  $\text{Al}^{27}$  ( $\sim 10$  gauss) and hence is not observed in paramagnetic resonance in ruby.

There are however some crystals in which the hyperfine broadening is sufficiently small to allow detection of strain effects in the ground state at very low concentrations. In this case one would expect smaller linewidths for the  $-\frac{1}{2} \rightarrow +\frac{1}{2}$  transition than for the  $\frac{1}{2} \rightarrow \frac{3}{2}$  transition. Furthermore, the linewidth would probably continue to decrease even at very low concentration since we would expect less strain when we decrease the impurity content.

For the optical transition, the concentration dependence of linewidth cannot depend on dipolar interaction since this is far too small. Dependence of strain on concentration would influence linewidth as described in the first part of this section. In addition, self-absorption will probably be a dominant factor for some transitions at certain conditions of strain and concentration. It is difficult on the basis of existing data to separate these effects.

Direct paramagnetic resonance in the  $^2E$  state should be of great value in answering some of these questions.

#### C. ADIABATIC VARIATION OF LOCAL FIELDS DUE TO LATTICE OSCILLATIONS

Thus far, no satisfactory theory has been advanced which will quantitatively explain the observed temperature-dependent linewidth. In this section we shall investigate a mechanism for line broadening in crystals which in certain instances, give reasonable agreement with both the temperature dependence and magnitude of the linewidths observed between  $50^\circ\text{K}$  and  $300^\circ\text{K}$ . We shall investigate the case of the  $^2E$  state of ruby in detail since this is an excellent example of where this theory should apply.

The mechanisms which cause the broadening of spectral lines may be divided into three classes. One class (a) includes all those mechanisms which reduce the lifetime of an excited state. This includes such

familiar line broadening causes as the natural lifetime and collision broadening. Another example of a line broadening mechanisms in this category would be non-radiative transitions in solids. The second class (b) includes all those interactions which broaden an energy level without affecting its lifetime. Inhomogeneous broadening in magnetic fields and the statistical strain broadening described in the previous section are stationary examples of this. However, it is not necessary for the energy to be rigorously stationary for a broadening mechanism to fall in class (b). So long as the adiabatic condition holds, it is possible for the interaction to cause slow variations in energy without affecting the lifetime of a state, as for example, quasi-static Stark broadening in gases. Doppler broadening does not conveniently fit into either previous class so we assign it to be the sole member of class (c). The velocity of ions in crystals is too low for Doppler broadening to be significant so we will not consider this further.

In this section we show that the "slow" variation in the energy levels can account for the temperature dependence of the linewidth in some instances.

The local electric field at the position of a given ion in a crystal depends on the instantaneous position of its neighbors. Due to the lattice vibrations the effective crystal field is a function of time and, moreover, varies throughout the crystal at a given instant. Let us determine if the time variation can be considered adiabatic. Let  $E = h\nu$  be the energy of the excited state relative to the ground (or terminal) state for the optical transition  $\langle \nu \rangle_{av} = \nu_0$ . The adiabatic condition requires

$$\frac{1}{h\nu_0^2} \frac{\partial E}{\partial t} = \frac{1}{\nu_0^2} \frac{\partial \nu}{\partial t} \ll 1.$$

Now the maximum frequency of the lattice vibrations is the Debye frequency  $\nu_D$  so that

$$\frac{1}{\nu_0^2} \frac{\partial \nu}{\partial t} \leq \frac{1}{\nu_0^2} (\nu_0 \nu_D) = \left( \frac{\nu_D}{\nu_0} \right).$$

For the case of ruby, which has an extremely high Debye frequency,  $\nu_D/\nu_0$  is less than 0.05. For most rare earth crystals this quantity is usually less than 0.005. Hence the variation of the local fields in crystals can be considered adiabatically slow even for temperatures near  $T_D = h\nu_D/k$ .

In our model then, the linewidth at moderate temperatures is caused by the "slow" variation of the energy of the excited states. The emission or absorption is reasonably assumed to be uncorrelated to the phase of the lattice vibrations. Of course, the vibrational period is very short compared to the time of measurement so that one always observes a broadened line about some average frequency.<sup>6</sup> The magnitude of the line broaden-

<sup>6</sup> As stated previously, the phase of the lattice vibrations varies throughout the crystal. This alone is sufficient to cause the broadening observed. The magnitude and temperature dependence of the broadening is the same whether one considers spatial or time variation.

ing is approximately equal to the amplitude of the energy variation of the excited state. We shall use this as our criterion for the magnitude of the linewidth for the present.

We now consider the details of our model for line broadening. To be precise let us consider a cubic crystal with 6 nearest neighbors. The vibrational potential may be written

$$v(t) = \sum_{i=1}^6 v_i' Q_i.$$

We need consider only the even vibrational modes  $Q_1 \cdots Q_6$  of the surrounding complex. For the present we restrict ourselves to transition element crystals. In this

case, lines which are sharp enough to be temperature broadened involve transitions between states whose energy difference depends on the crystal fields to second or higher order.

We can compute the expectation value of  $v$  in the usual way:

$$\langle v \rangle = \sum_{i=1}^6 v_i' \langle |Q_i|^2 \rangle^{\frac{1}{2}},$$

where  $\langle v \rangle$  is still to be treated as an operator. Now since we are interested only in second order effects in transition elements we can express the magnitude of the oscillatory energy shift (which is approximately equal to the linewidth<sup>7</sup>) as

$$\langle \Delta \mathcal{E}_T \rangle = \sum_{k, \Gamma', \gamma', m'} \frac{\langle \Gamma \gamma m, n_k | v_i' Q_i | n_k \pm 1, \Gamma' \gamma' m' \rangle \langle \Gamma' \gamma' m', n_k \pm 1 | v_i' Q_i | n_k, \Gamma \gamma m \rangle}{E(\Gamma) - E(\Gamma')}. \quad (3)$$

The  $Q_i$  must still be expanded in the lattice coordinates  $a_k, a_k^\dagger$  (step-up and step-down operators). The  $n$  are lattice oscillator occupation numbers.

We have

$$Q_i = \sum_k b_{ik} (a_k + a_k^\dagger), \quad (4)$$

where the  $b_{ik}$  are given in reference 8.

To carry this computation further requires the introduction of a specific ionic system. We will shortly consider the case of the  ${}^2E$  state of ruby in detail and then consider the application of this model to rare earths. But first we must deal with a rather subtle point.

The substitution of the Eq. (4) for  $Q_i$ , into Eq. (3) leads to an expression of the form (where we separate ionic and lattice coordinates)

$$\langle \Delta \mathcal{E}_T \rangle = \sum_i \frac{|\langle \Gamma \gamma m | v_i' | \Gamma' \gamma' m' \rangle|^2}{E(\Gamma) - E(\Gamma')} \times \sum_k |b_{ik}|^2 \langle \cdots | a_k^\dagger a_k + a_k a_k^\dagger | \cdots \rangle. \quad (5)$$

If we proceed in this straightforward manner we see that the zero-point oscillations are included in the final result; indeed for temperatures below the Debye temperature the major contribution to Eq. (5) would be from the zero-point fluctuations since most lattice oscillator modes are unoccupied. (A linewidth of about 100 wave numbers would be predicted at zero degrees Kelvin if this contribution is included.) Several writers have attempted to estimate the linewidth using an adiabatic model and *including* the zero-phonon-field fluctuations contribution. This type of approach is fundamentally incorrect. While the zero-point fluctua-

tions of the electromagnetic field can affect the linewidth (for example, natural linewidth) it does so only through reduction of the lifetime of the excited state. The lifetime is not affected, however, in our model since the radiative lifetime of most fluorescent states is  $> 10^{-5}$  sec and the fluorescent efficiency, of the states we consider, is quite high. One must therefore subtract the contribution of the zero-point fluctuations. We can put this argument into a more rigorous form.

The contribution of just the zero-point fluctuations in Eq. (5) is

$$\sum_i \frac{|\langle \Gamma \gamma m | v_i' | \Gamma' \gamma' m' \rangle|^2}{E(\Gamma) - E(\Gamma')} \sum_k |b_{ik}|^2 \langle 0000 | a_k a_k^\dagger | 0000 \rangle. \quad (6)$$

This expression is in exact analogy to the self-energy of the electron in nonrelativistic electrodynamics. Indeed this is exactly the expression one obtains if he attempts to compute the self energy of the ion in the phonon field. (We of course have considered the interaction of  $\Gamma$  with only one manifold,  $\Gamma'$ , here. The exact self-energy requires summing over all states of the system.) As in the analogous case in electrodynamics this term should be subtracted from the Hamiltonian preferably by mass renormalization. The only effect it can have is the so-called level shift which could lead to a Lamb effect.

We shall not pursue these arguments any further, contending ourselves with the justification for subtracting the zero-field contributions. It is interesting to note that the evaluation of Eq. (6) leads to a finite result. This is of course due to the fact that there is only a finite number of lattice modes in contradistinction to the infinite number of modes in the electromagnetic counterpart. The fact that Eq. (6) is finite allows for unambiguous subtraction of the self-energy from Eq. (5).

As a final word, I would like to point out that in a more fundamental approach, one would write out the

<sup>7</sup> If we were to attempt to complete analogy to the previous section one would have the matrix element of the operator  $(v_i Q_i) K$ . However, this operator has no diagonal elements due to the properties of  $Q_i$ . Hence the physically observed contribution must come from  $\langle Q_i v_i \rangle^2$ .

<sup>8</sup> J. H. Van Vleck, Phys. Rev. 57, 426 (1940).

entire effective Hamiltonian for the system. The next step would be subtract the self-energy terms, Eq. (6), and finally to interpret the remainder of (3) as an adiabatic strain term. The "real" phonons have a definite phase unlike the zero-point fluctuation which must not be considered time dependent.

#### D. CALCULATION OF TEMPERATURE DEPENDENCE OF THE LINEWIDTH OF ${}^2E({}^2\Gamma_3)$ STATE OF RUBY

For the  ${}^2E$  state of ruby, Eq. (5) reduces to

$$\frac{|\langle {}^2E\gamma m | v_4' | {}^2T_2\gamma m \rangle|^2}{E({}^2E) - E({}^2T_2)} \sum_k 2|b_{4k}|^2 \langle n_k | a_k^\dagger a_k | n_k \rangle. \quad (7)$$

We have defined our zero-order wave functions to diagonalize the natural trigonal field of ruby. This is the reason that only the  $Q_4v_4'$  of Eq. (5) was required above (where  $Q_4$  and  $v_4'$  have the same symmetry and orientation as the natural trigonal field). Only the interaction of  ${}^2T_2$  with  ${}^2E$  was considered since this is the nearest state (7500  $\text{cm}^{-1}$ ) which can interact directly with  ${}^2E$  through the lattice vibrations.

If we average over the phase and propagation directions of the lattice waves we get

$$\begin{aligned} |b_{4k}|^2 &= 4R^2\hbar\nu/60Mv^2, \quad (\text{longitudinal}) \\ &= 3R^2\hbar\nu/60Mv^2, \quad (\text{transverse}) \end{aligned} \quad (8)$$

where  $R$  is the distance from the paramagnetic ion to the neighboring ligands,  $M$  is the crystal mass,  $v$  is the velocity of sound, and  $\nu$  is the phonon frequency. Equation (7) now becomes

$$\langle \delta\mathcal{E}_T \rangle = \frac{|\langle {}^2E\gamma m | Rv_4' | {}^2T_2\gamma m \rangle|^2}{E({}^2E) - E({}^2T_2)} \sum_\nu \frac{6\hbar\nu}{3Mv^2} n_\nu. \quad (9)$$

We have neglected the longitudinal mode in Eq. (9) since it has a larger velocity than the transverse modes.

We use the strong field approach of Tanabe and Kamimura<sup>5</sup> to evaluate the matrix element in  $Rv_4'$ . By methods similar to that used in reference 3

$$|\langle {}^2E1+\frac{1}{2} | Rv_4' | {}^2T_21+\frac{1}{2} \rangle|^2 = 6|\langle l\xi | v_\xi(T_2) | l\eta \rangle|^2. \quad (10)$$

The function  $|l\xi\rangle$  and  $|l\eta\rangle$  are just the proper functions of an electron with azimuth quantum numbers  $+1$  and  $-1$ .

The form of the oscillating potential for a cubic complex is well known.<sup>9</sup> In our case

$$v_\xi(T_2) = e^2 \left\{ -\frac{6xy}{R^3} + \frac{15xyr^2}{R^5} - \frac{35}{2R^6}(x^3y + xy^3) \right\}, \quad (11)$$

where  $x$ ,  $y$ ,  $z$ , and  $r$  are ionic coordinates. If we perform

<sup>9</sup> J. H. Van Vleck, J. Chem. Phys. 7, 76 (1939).

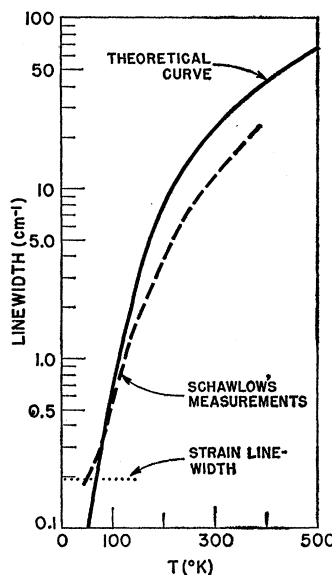


FIG. 2. Linewidth of the  ${}^2E$  states of ruby.

the indicated integration we obtain

$$\begin{aligned} &|\langle {}^2E1+\frac{1}{2} | Rv_4' | {}^2T_21+\frac{1}{2} \rangle|^2 \\ &= \frac{216}{49} e^4 \left( \frac{\langle r_0^2 \rangle_{\text{av}}}{R^3} - \frac{5}{9} \frac{\langle r_0^4 \rangle_{\text{av}}}{R^5} \right)^2. \end{aligned} \quad (12)$$

We can replace the summation in Eq. (9) by an integral if we introduce the density function  $\rho(\nu) = 4\pi\nu^2 V/v^3$ . Also we can use the relation

$$\bar{n}_\nu = [\exp(\hbar\nu/kT) - 1]^{-1}.$$

The rest of the computation follows reference 3 closely. We obtain finally

$$\begin{aligned} \langle \delta\mathcal{E}_T \rangle &= 11.2 \frac{V\hbar}{Mv^5} \left( \frac{kT_D}{h} \right)^4 \frac{e^4 (\langle r_0^2 \rangle_{\text{av}}/R^3 - 5\langle r_0^4 \rangle_{\text{av}}/9R^5)}{|E({}^2E) - E({}^2T_2)|} \\ &\times \left[ \left( \frac{T}{T_D} \right)^4 \int_0^{T_D/T} \frac{x^3 dx}{e^x - 1} \right] \\ &\cong 10^3 \left( \frac{T}{T_D} \right)^4 \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx \quad (\text{cm}^{-1}). \end{aligned} \quad (13)$$

Figure 2 shows the predicted linewidth as a function of temperature for ruby. The dashed curve gives the linewidth versus temperature as measured by Schawlow. The horizontal line gives the observed zero-temperature linewidth.

At 100°K our theory predicts a linewidth of 0.6  $\text{cm}^{-1}$  compared to the value 0.5  $\text{cm}^{-1}$  obtained in Schawlow's experiments.<sup>10</sup> The general character of the two curves are quite similar although the rise of linewidth with

<sup>10</sup> A. L. Schawlow (private communications). I am grateful to Dr. Schawlow for making the experimental data in Fig. 2 available to me before publication.

temperature is somewhat more rapid in the theoretical curve.

The over-all agreement between theory and experiment is quite good especially considering the crudeness of the model used. The fact that the theoretical curve lies above the experimental curve can be explained by the deviations of the oscillator spectrum from the simple one assumed.

It would be profitable to discuss the analytic behavior of Eq. (13) briefly. For temperatures much less than the Debye temperature ( $T/T_D < 0.05$ ) the upper limit of the integral may be taken as infinity so that

$$\left(\frac{T}{T_D}\right)^4 \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx \rightarrow \frac{6.48}{T_D^4} T^4,$$

which is reminiscent of the black body equation. For temperatures much greater than the Debye temperature (which is unrealistic in the case of ruby but holds for room temperature for many rare earth crystals) the quantity  $x^3(e^x - 1)^{-1}$  may be approximated by  $x^2$ :

$$\left(\frac{T}{T_D}\right)^4 \int_0^{T_D/T} x^2 dx = \frac{T}{3T_D}.$$

### E. CONCLUSIONS

The previous theory should apply to most energy levels in paramagnetic solids which do not interact with crystal field in first order and do not relax too rapidly to neighboring states. The second condition will

be fulfilled at low temperatures when the state in question is separated from the next lowest state by an energy either much less than the Debye limit or several times greater than the Debye limit. Other effects such as the variation of  $B$  or  $\zeta$  with the vibrating fields are special cases of the theory presented in Sec. C.

The case of  $\text{Cr}^{3+}$  in  $\text{MgO}$  is also of some interest.

The vibrational distortions cannot split the  ${}^2E$  states to the order considered by Schawlow *et al.* This is because the  $Q_i$  do not have any diagonal matrix elements. The tetragonal modes  $Q_{2,3}$  also interact with  ${}^2E$  only through configuration interactions. This effect will be small compared to that of the trigonal vibrations because of the large energy denominator. A contribution from the cubic mode  $Q_1$  may occur through the configuration interaction  $t^3 \rightarrow te^3$  but again the energy denominator is larger than for  $Q_4'$ . The Racah parameter  $B$  will be affected by  $Q_1$  and this can lead to line broadening. It is difficult at this point to compare this effect to the broadening due to  $Q_4'$ . If the latter effect is dominant (and I believe it is), we may use the results of Eq. (13) with only minor changes of the parameters. Actually no very significant difference is found in the parameters for the two cases so that we may assume the results of Eq. (13) hold fairly well for  $\text{MgO}:\text{Cr}$ . However, the zero-temperature linewidth in  $\text{MgO}:\text{Cr}$  should be somewhat smaller than that of ruby for equal strains.

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