Cr³⁺ Fluorescence in Garnets and Other Crystals*

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The results of a study of the sharp-line fluorescence of Cr³⁺ in a number of crystals is presented. The host crystals were several diamagnetic garnets, a spinel, and emerald. The results are used to discuss two aspects of the sharp-line energy levels. First, some of the dynamical aspects are considered. The measurements of the temperature dependence of the sharp no-phonon R-line positions, linewidths, and efficiencies are in reasonable agreement with the existing theory. The theory assumes a simple form for the interaction of the Cr³⁺ energy levels with the phonons and uses a Debye density of states. The phonon-assisted radiation is also discussed. Second, some of the static aspects of the energy levels are considered. The splittings between the no-phonon R lines along with splittings of the ground states of the Cr³⁺ in the same crystals are compared with the predictions of existing theories. Here the agreement is very poor. The experimental data show the difference between the Cr³⁺ energy levels, when odd terms in addition to usual even crystal-field terms exist. The data also indicate some large nonlinearities between the energy-level splittings and the crystal field.

INTRODUCTION

THE energy levels of the transition-series ion Cr³⁺ ($3d^3$ configuration) in octahedral symmetry have been studied extensively. Recent theoretical work on these energy levels has been carried out by Sugano and Peter[1] for Cr³⁺ in ruby. The calculation allowed for configuration mixing and covalency of the $3d^3$ electrons and predicted the positions, the splittings, and the g values of many of the energy levels. Reasonable agreement with experiment was obtained. The calculations were performed[1,2] assuming the Cr³⁺ ions see inversion symmetry. This has been criticized[3] since in ruby the point symmetry is really $C_3(3)$, i.e., the Cr³⁺ ions do not see inversion symmetry, and it has been shown that this has large effects on at least the ground-state splitting. Thus, the good agreement in Ref. 1 is somewhat suspect.

In this paper data are presented on the optical emission from Cr³⁺ in several garnets, emerald, and the spinel ZnAl₂O₄. The Cr³⁺ in most of the compounds sees inversion symmetry. The emission consists of sharp no-phonon lines (R lines, which in ruby give rise to laser action) and much broader phonon-assisted radiation. The positions, linewidths, quantum efficiencies, and splittings of the R lines (splittings of the ²E state) have been measured as a function of temperature. The data are considered from two somewhat unrelated points of view. First, the temperature dependence of the line widths and positions is compared to recent theoretical calculations[4-7] of these quantities. Second, the splittings

of the ground ($^4A_2$) state and the splittings of the excited (^2E) state are compared to theory.[1-3] The agreement is poor. It is experimentally apparent that the odd terms in the crystal field cause ruby to behave differently from the garnets. Thus, theories of the energy levels that ignore the odd crystal-field terms[1,2] should aim at reproducing the magnitude and sign of the splittings in the garnets rather than ruby. However, experimentally one finds the energy-level behavior is quite complicated. The splitting of the ^2E state is not proportional to the $^4A_2$ state splitting for large $^4A_2$ splittings.

EXPERIMENTAL PART

The garnet crystals used were grown by published techniques.[8] The Ga garnet single crystals accepted the Cr³⁺ more readily than the Al garnets and thus appeared slightly green while the Al garnets were essentially colorless. From crystal-chemistry considerations one would expect the Cr³⁺ to occupy the octahedral 16(a) sites in the garnet rather than the tetrahedral 24(d) sites.[9] (The space group of the garnets is $O_h^{10} - Ia3d$.) Also the spectra from Cr³⁺ in tetrahedral sites would be quite unlike the observed spectra. This is because the sign of the cubic-field splitting reverses between tetrahedral and octahedral sites causing the strong-field energy levels to invert. The emerald crystals used were both synthetic and natural. No differences were seen. The ZnAl₂O₄ was grown by a flux technique.[10]

The crystals were excited with a mercury arc filtered by a CuSO₄ solution, and the emission was detected with a cooled infrared-sensitive photomultiplier. A Perkin-Elmer 99G monochromator ($\approx \frac{1}{2}$ Å resolution) was used for most of the spectral measurements. The high resolu-measurements were made on a one-meter Jarrell-Ash Ebert grating monochromator which could resolve better than 0.1 Å.

* A preliminary account of some of this work has appeared in Bull. Am. Phys. Soc. **8**, 215 (1963).

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[3] J. O. Artman and J. C. Murphy, *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1963), p. 634. See also other papers by these authors: J. Chem. Phys. **38**, 1544 (1963) and Phys. Rev. **135**, 1622 (1964).

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[6] D. E. McCumber and M. D. Sturge, J. Appl. Phys. **34**, 1682 (1963). See also D. E. McCumber, J. Math. Phys. **5**, 221, 508 (1964).

[7] B. Z. Malkin, Fiz. Tverd. Tela **5**, 3088 (1963) [English transl.: Soviet Phys.—Solid State **5**, 2262 (1964)].

[8] J. W. Nielsen, J. Appl. Phys. **31**, 515 (1960).

[9] M. A. Gilleo and S. Geller, J. Appl. Phys. **29**, 380 (1957); S. Geschwind and J. W. Nielsen, Bull. Am. Phys. Soc. **5**, 252 (1960).

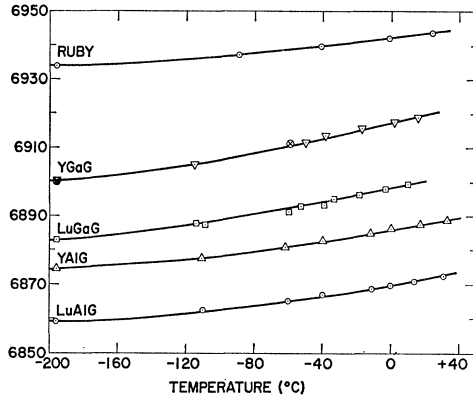[10] E. A. Giess, J. Am. Ceram. Soc. **47**, 388 (1964).

FIG. 1. The wavelength of the lower energy R lines versus temperature for the garnets and ruby.

Efficiency measurements were made as previously described.[11]

RESULTS AND DISCUSSION

A. Line Position, Width, and Intensity

Table I lists the materials that have been studied as well as the separation between the R lines and their

TABLE I. General summary of the results and of previously reported results.[a]

Lattice (abbreviation)	Site symmetry of Cr^{3+}	Position of R lines at 77°K (Å)	R line splitting $(2\bar{A}-\bar{E})$ at 77°K (cm⁻¹)	$2D$ (cm⁻¹)
Al_2O_3 (ruby)	3	6934.0[b] 6920.1	+29.4[b]	−0.383[c] |0.38|
$Y_3Ga_2(GaO_4)_3$ (YGaG)	$\bar{3}$	6900.4 6887.7	±26.7[d]	+0.697[e] |≈0.63|[f]
$Lu_3Ga_2(GaO_4)_3$ (LuGaG)	$\bar{3}$	6882.8 6874.2	18.1	
$Y_3Al_2(AlO_4)_3$ (YAlG)	$\bar{3}$	6874.0 6864.7	19.6	|0.524|[g] |0.53|
$Lu_3Al_2(AlO_4)_3$ (LuAlG)	$\bar{3}$	6858.7 6852.9	12.4	|0.52|
$ZnAl_2O_4$ (spinel)	$\bar{3}m$	6860.4[h] 6857.2	|6.9|	+1.78[i] |≈1.7|[f]
$Be_3Al_2(SiO_3)_6$ (emerald)	32	6821.6[j] 6792.7	−62.4	−1.74[k]

ᵃ Results of previous work on Cr^{3+} in $LaAlO_3$ and $MgAl_2O_4$ are used later. References to the original work are: $LaAlO_3$—$2\bar{A}$—$\bar{E}$ = \|5.4 cm⁻¹\|, L. Couture, F. Bruntiere, F. Forrat, P. Tevoux, Compt. Rend. **256**, 3046 (1963). $2D$ = \|0.112 cm⁻¹\|, D. Kiro, W. Low, and A. Zusman, *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1963), p. 44. $MgAl_2O_4$—$2\bar{A}$—$\bar{E}$ = \|6.0 cm⁻¹\|, O. Deutschbein, Z. Physik **77**, 489 (1932). $2D$ = +1.83 cm⁻¹, S. B. Berger, J. Appl. Phys. **36**, 1048 (1965).
ᵇ S. Sugano and I. Tsujikawa, J. Phys. Soc. (Japan) **13**, 899 (1958).
ᶜ See J. W. Orton, Rept. Progr. Phys. **22**, 204 (1959).
ᵈ The sign is obtained from Ref. 25.
ᵉ S. Geschwind and J. W. Nielsen, Bull. Am. Phys. Soc. **5**, 252 (1960).
ᶠ These values, written with an ≈ sign, are obtained here optically but the lines cannot be well resolved and the ground-state splittings are thus very approximate.
ᵍ J. W. Carson and R. L. White, J. Appl. Phys. **32**, 1787 (1961).
ʰ These results are not in good agreement with some values published some time ago: O. Deutschbein, Z. Physik **77**, 489 (1932).
ⁱ J. E. Drumbeller, K. Locher, and F. Waldner, Helv. Phys. Acta **37**, 628 (1964). The sign has been determined by J. Overmeyer (unpublished).
ʲ In good agreement with other work: Ref. 27.
ᵏ J. E. Geusic, M. Peter, and E. O. Schulz-Du Bois, Bell System Tech. J. **38**, 291 (1959).
¹¹ G. Burns and M. I. Nathan, J. Appl. Phys. **34**, 703 (1963).

positions at 77°K. Figures 1 and 2 show the temperature dependence of the position, linewidth, and R line efficiency η_R ($\equiv$ intensity of the R lines/total intensity in the red) for the four garnets.

The R line efficiency for the garnets is considerably smaller than the low-temperature values of greater than 50% that have been found for ruby.[11,12] The complete temperature dependence of η_R for the two Lu garnets has not been measured. However, at 77°K and room temperature η_R for Lu Al garnet (LuAlG) is the same as for Y Al garnet (YAlG). For LuGaG at 77°K and room temperature η_R is the same as for Y Ga garnet (YGaG). The two Ga garnets were only very slightly green and the Al garnets were colorless, so self-absorption corrections[12,13] are probably small. For emerald $\eta_R \approx 40\%$ at 77°K and is very small at room temperature. For $ZnAl_2O_4$, η_R is small even at 77°K. Thus a Cr^{3+} laser made from any of the materials studied here would be inferior to ruby where η_R is high even at room temperature.

The most salient feature of the temperature dependence of the line position and width as in Figs. 1 and 2 is that the two Ga garnets behave similarly to each other. The two Al garnets also behave similarly to each other. However, the Al compounds have a smaller temperature derivative than the Ga compounds. This fact is clearly brought out in Fig. 3 which is a plot of the line shift relative to its position at 4.2°K.

To understand the temperature of the sharp Cr^{3+} emission several ideas have been developed and applied.[4–7,14–17] The Hamiltonian describing the impurity ion in a lattice with phonons can be written

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_p+\mathcal{H}_I, \tag{1}$$

where $\mathcal{H}_0$ describes the ion in a static crystal field, $\mathcal{H}_p$ describes the phonons, $\mathcal{H}_I$ describes the interaction of the ion with the phonons, which for dispersionless acoustic phonons is

$$\mathcal{H}_I=\sum_k (A/v)\omega_k^{1/2}\xi_k+\sum_{kk'} (B/v^2)\omega_k^{1/2}\omega_{k'}^{1/2}\xi_k\xi_{k'}, \tag{2}$$

where A and B are the linear and quadratic coupling coefficients, ξ_k is a normal coordinate of wave vector k and frequency ω_k, and $v=\omega_k/k$ is a constant. Using this approximation for $\mathcal{H}_I$ the shift of position of the no-phonon line with temperature, $\Delta E(T)\equiv E(0)-E(T)$, and the temperature dependence of the linewidth $\Delta\Gamma(T)\equiv\Gamma(T)-\Gamma(0)$ can be written for each no-phonon

¹² D. F. Nelson and M. D. Sturge, Phys. Rev. **137**, A1117 (1965).
¹³ F. Varsanyi, D. L. Wood, and A. L. Schawlow, Phys. Rev. Letters **3**, 544 (1959).
¹⁴ G. F. Imbusch, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, Phys. Rev. **133**, A1029 (1964).
¹⁵ W. M. Yen, W. C. Scott, and A. L. Schawlow, Phys. Rev. **136**, A271 (1964).
¹⁶ R. H. Silsbee, in *Proceedings of the Third International Congress on Quantum Electronics* (Columbia University Press, New York, 1964), p. 773.
¹⁷ A. L. Schawlow, in *Proceedings of the Third International Congress on Quantum Electronics* (Columbia University Press, New York), p. 645.

line as[6]

$$\Delta E(T) = \alpha \int_0^\infty \rho(\omega)\eta\frac{d\omega}{2\pi},$$

$$\Delta\Gamma(T) = \bar\alpha \int_0^\infty [\rho(\omega)]^2\eta(\eta+1)\frac{d\omega}{2\pi}. \tag{3}$$

$$\eta = [\exp(\hbar\omega/KT)-1]^{-1}.$$

$\rho(\omega)$ is an effective density of states associated with the form of $\mathcal{H}_I$. Since the relation between ω and k was taken as linear, $\rho(\omega)$ is the Debye density of states. At temperatures high enough to populate the many optical modes or the parts of the acoustic branches where the dispersion is large, Eq. (2) should be a poor approximation. The α in Eq. (3) involves[6,14,15] the square of the coupling coefficient A plus linear terms in the coefficient B. The $\bar\alpha$ term involves α^2 plus A^4 and B^2 types of terms. For a Debye model $\rho(\omega) = \hbar\omega^3/2\pi\rho_m\bar v^5$ for $0<\omega<\omega_D$ and zero above ω_D where the upper cutoff frequency is given in terms of an effective Debye temperature, $\hbar\omega_D = kT_D$, with ρ_m the mass density, $\bar v$ the average sound velocity. Then Eqs. (3) can be written as

$$\Delta E(T) = \alpha\left(\frac{T}{T_D}\right)^4 \int_0^{T_D/T} dx\, x^3[\exp(x)-1]^{-1}$$

$$\Gamma(T) = \bar\alpha\left(\frac{T}{T_D}\right)^7 \int_0^{T_D/T} dx\, x^6 \exp(x)[\exp(x)-1]^{-2}. \tag{4}$$

Equation (4) can be used to fit the experimental $\Delta E(T)$ data where α and T_D are treated as adjustable parameters, and $\Gamma(T)$ can be fitted with $\bar\alpha$ as a parameter. Using the Debye spectrum the data for[6] Cr^{3+} in Al_2O_3, for[14] V^{2+} and Cr^{3+} in MgO and[18] for V^{2+} and Mn^{4+} in
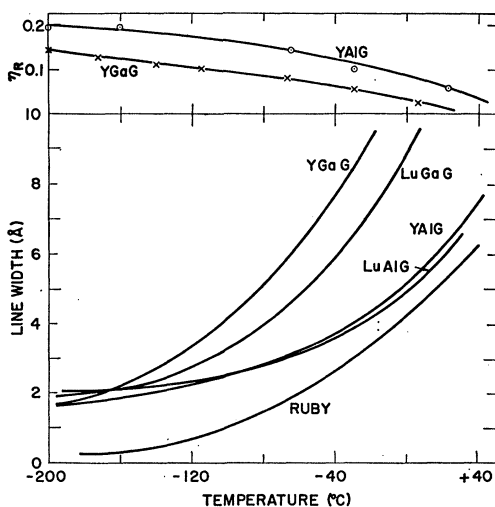

FIG. 2. The linewidths and R-line efficiencies η_R versus temperature.

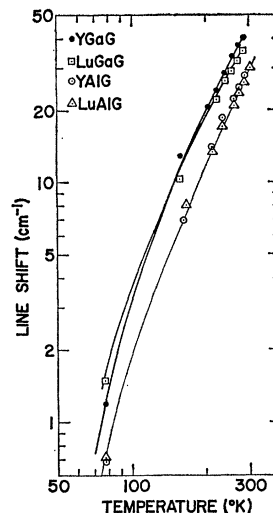[18] M. D. Sturge (private communication).

FIG. 3. Shift of the lower-energy R line below its position at 4.2°K for the four garnets. The curves are calculated from Eq. (4).

Al_2O_3 has been fitted fairly well. All of these fits give values of T_D that are not equal to the Debye temperature as normally defined in the thermal Debye theory. This is not too surprising in view of the approximate nature of the interaction Hamiltonian Eq. (2). For the garnets, the $\Delta E(T)$-versus-T curves of Fig. 3 can also be fitted with Eq. (4). The values of T_D that are required are: YAlG(560°K), YGaG(530°K), LuAlG(560°K), and LuGaG(440°K). $\Gamma(T)$ was not fitted for the garnets because of the poor data that were obtained. As can be seen in Fig. 2 the residual linewidth at low temperatures was very wide in the crystals and the intensity dropped off very rapidly at high temperatures. Thus, there is only a very small region over which one could fit the data, and almost any parameters could be used for such a fit.

These values of T_D for the garnets are in the same general range as the Debye constant obtained from specific heat measurements. Since the Debye constants for the Al and Ga compounds are not available the values will be compared with the isomorphous iron compounds. For YIG and LuIG, 570°K and 460°K, respectively, are obtained.[19] For the YAlG and LuAlG, similar but larger values of the thermal Debye constant would be expected. However, to fit the $\Delta E(T)$ data for the two Al garnets the same values of T_D were required. For the YGaG and LuGaG compounds, since the masses of the atoms are very similar to the YIG and LuIG compounds, one would expect values slightly lower than the corresponding iron-compound results quoted above. (For a simple model one expects the Debye constant $\propto (m)^{-1/2}$ where m is the average mass of the atoms per unit cell.) This is what is observed for the values of T_D. In conclusion it appears that the simple form of the interaction dispersionless acoustic Hamiltonian, Eq. (2), with a Debye density of states can fit the temperature dependence of the data.

In addition to the R lines, Cr^{3+} also emits radiation

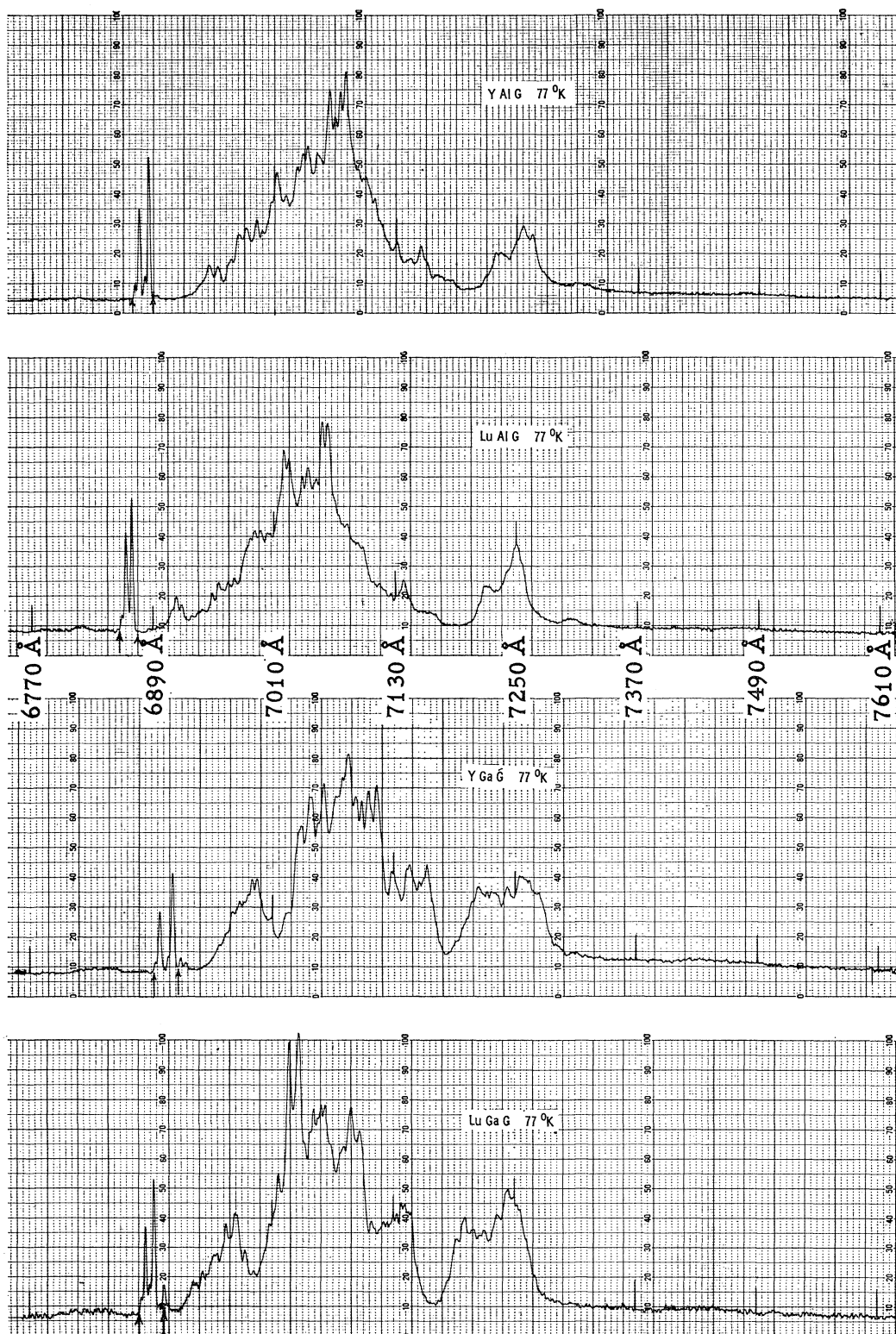[19] A. B. Harris and H. Meyer, Phys. Rev. 127, 101 (1962).

FIG. 4. Emitted intensity versus wavelength. The phonon-assisted radiation of the four garnets can be seen. The R lines can also be seen between the two arrows. The gain was reduced between the arrows. The marks occur every 120 Å.

due to phonon-assisted transitions between the ^2E and $^4A_2$ state. Figure 4 shows the phonon-assisted spectra for the four garnets at 77°K. The quantum efficiency of the sharp-line fluorescence is low because much of the radiation is phonon-assisted radiation. As the temperature is raised the phonon population increases. This causes the phonon-assisted radiation to grow at the expense of the sharp lines even though the total emission in the red is constant to above 100°C. This result is similar to that found in ruby.[11]

There has been some tendency in the literature[14] to associate $\rho(\omega)$ in Eq. (3) with the phonon-assisted spectra. However, this is not consistent with the observations as the following discussion will show.

Since an impurity ion is highly localized, one would expect it, on the simplest basis, to be able to couple to phonons with all k vectors. So optical and acoustic modes should contribute to the phonon-assisted radiation. In garnets, where there are three acoustic and 237 optical branches, it is probable that the many peaks in the phonon-assisted spectra (see Fig. 4) are associated with the many optical modes.

In at least one case, $Pr^{3+}:LaCl_3$, there does not appear to be any evidence of acoustic modes in the experimental phonon-assisted data.[20] Rather, the authors argue that the data are consistent with a $k=0$ selection rule. Pr^{3+} in $LaCl_3$ is a particularly favorable case because localized modes should not be important since the mass difference between Pr^{3+} and La^{3+} is relatively small and one would expect the force constants for the two ions to be very similar. However, even in this case, the intensities of the various lines in the phonon-assisted radiation are entirely different for the transition from the ground state to the $^3P_0$ state than from the corresponding lines in the transition to the $^3P_1$ state. $Pr^{3+}:LaF_3$ is a system very similar to $Pr^{3+}:LaCl_3$ but more complicated results are found. The observed phonon-assisted spectra for the transition from the ground state to the $^3P_0$ shows many sharp peaks.[15] Some of the peaks of the phonon-assisted spectra correspond to the energies observed in infrared lattice-absorption measurements and Raman experiments[21] and thus correspond to the $k=0$ part of the optical branches. However, even in this case two of the Raman lines and one of the infrared lattice lines correspond to energies higher than observed[15] for phonon-assisted radiation.

The phonon-assisted radiation of Cr^{3+} in emerald has a number of well-defined lines as can be seen in Fig. 5. This emission can be compared to the published infrared lattice-absorption data.[22] The position of the peaks of the infrared data are shown in the figure. As can be seen there is not a one-to-one correspondence between the two sets of data.

[20] I. Richman, R. A. Satten, and E. Y. Wong, J. Chem. Phys. 39, 1833 (1963).
[21] H. H. Caspers, R. A. Buchanan, and H. R. Markin, J. Chem. Phys. 41, 94 (1964).
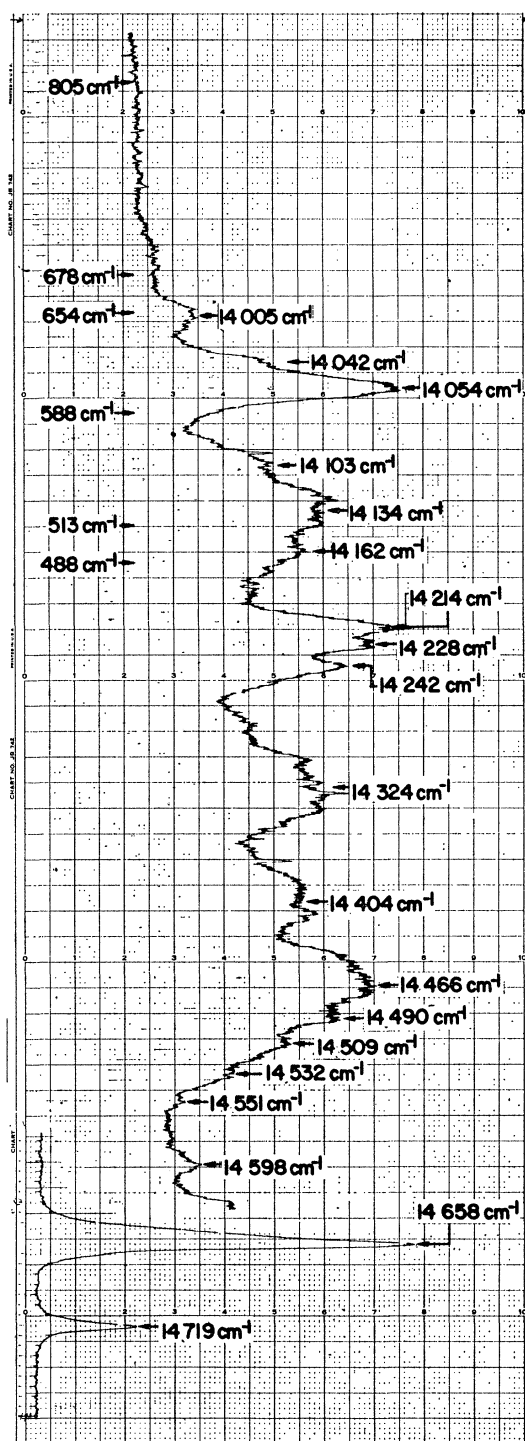[22] J. Vincent-Geisse and J. Lecomte, Z. Physik 173, 149 (1963).

FIG. 5. The phonon-assisted radiation from emerald at 77°K. The two R lines can also be seen. (The sweep speed for R lines and phonon-assisted radiation was the same, but to get the R lines on the paper the slit width for the phonon = 200 μ. The slits for the R lines = 40 μ.) The position of the lines is given in wave numbers, although the sweep is approximately linear in wavelength. The peaks in the lattice-vibration spectra, as measured in Ref. 22, are also given on the lower part of the figure. They were positioned by subtracting their energies from the lower-energy R line.
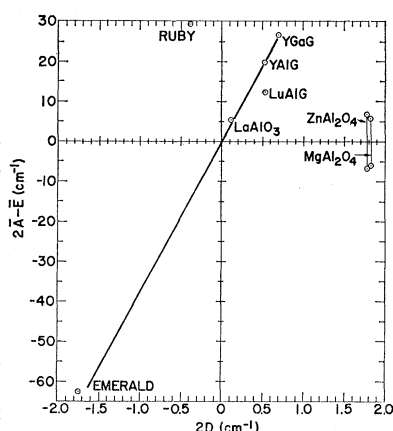
FIG. 6. A plot of the R-line splitting $2\bar{A}-\bar{E}$ versus the ground-state splitting $2D$ for Cr^{3+} in several lattices. The data or references to previously published data are in Table I.

The results show that there is as yet no demonstration of a simple correspondence between the phonon-assisted radiation that one observes as side bands to sharp-line optical spectra and the phonon density of states. A careful look at the selection rules is needed. Also, the approach of calculating the pseudolocalized modes[23] may be able to explain the details of the phonon-assisted radiation.

B. R-Line and Ground-State Splittings

In this section the relation between the splittings of the excited state (^2E state) and the ground state ($^4A_2$ state) is discussed. Theoretical work[1–3,24–26] on these splittings is fairly detailed. However, some of the workers have suggested that the agreement of theory with the ruby data is a validation for a theory. This has been criticized,[3] and it has been shown that in ruby the odd terms in the crystal field contribute important terms to at least the ground-state splitting.[3] Here it will experimentally be shown that the splittings of the ground state and ^2E states in ruby do indeed behave quite differently from the splitting observed when the Cr^{3+} sees inversion symmetry. However, a further complication arises, namely, even in crystals where the Cr^{3+} sees inversion symmetry the R-line splitting and the ground-state splitting are not simply linearly related.

If the symmetry is lower than cubic, the excited ^2E level will split into two levels, $2\bar{A}$ and $\bar{E}$. In ruby the $\bar{E}$ is lower in energy by 29 cm^{-1}. (One can tell which level is which by polarized-absorption measurements[2] as was also done here. The result is emerald has a sign

of the ^2E splitting opposite to that of ruby.) Also, for noncubic symmetry, the ground ($^4A_2$) state which has $S = \frac{3}{2}$ will split into two Kramers doublets with $m_S = \pm\frac{3}{2}$ and $\pm\frac{1}{2}$. The spin Hamiltonian for Cr^{3+} with this zero field splitting $2D$ is

$$\mathcal{H} = g\beta H \cdot S + D[S_z^2 - S(S+1)/3]. \qquad (5)$$

The concern here will be with the values of D. (See Table I.) For cubic symmetry $D = 0$ and it is an odd function of the strain.

Figure 6 is a plot of the energy difference between the excited state and the ground state, i.e., $2\bar{A}-\bar{E}$ vs $2D$. Each point represents data taken on Cr^{3+} in one compound. References to previous original work are in the footnotes of Table I. Here we mention how some of the new values and signs were determined. The sign of the R line splitting in emerald was determined by polarized absorption as mentioned above. The magnitude of the ground state splitting in LuAlG was determined from the splitting of the R lines. As can be seen in Fig. 7 the ground-state splitting could be resolved in good strain-free samples, which were recently obtained. The sign of the R line splitting has been determined in only one garnet[27] but is assumed to be the same for the other garnets for both experimental and theoretical reasons.[28,29] The signs for the R line splittings in the spinels are at present unknown. The sign of neither the R lines nor the ground state splitting is known for Cr^{3+} in LaAlO$_3$, but in Fig. 6 a positive sign for both is assumed.

To compare these experimental results to theory it is

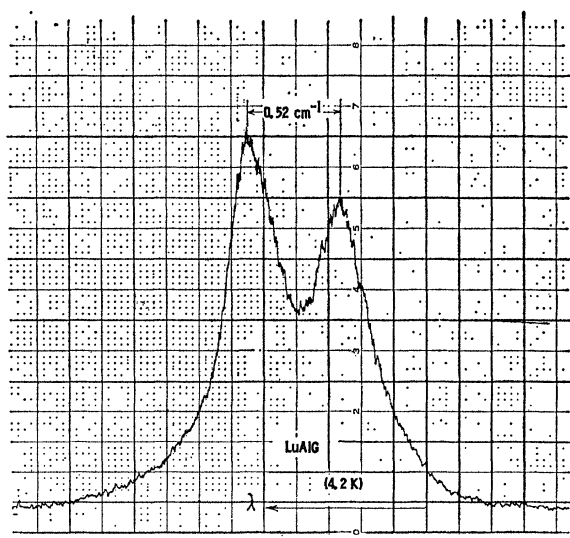FIG. 7. The lower-energy R line of Cr^{3+} in LuAlG at 4.2°K. The ground-state splitting is shown.

[23] See, for example, two papers by W. E. Bron and M. Wagner, Phys. Rev. 139, A223, A243 (1965).

[24] L. I. Lohr, Jr. and W. N. Lipscomb, J. Chem. Phys. 38, 1607 (1963).

[25] R. M. Macfarlane, J. Chem. Phys. 39, 3118 (1963); 42, 442 (1965).

[26] H. Kamimura, Phys. Rev. 128, 1077 (1962).

[27] D. M. Sturge, Bull. Am. Phys. Soc. 8, 439 (1963).

[28] W. J. Nicholson and G. Burns, Phys. Rev. 133, A1568 (1964).

[29] D. L. Wood, J. Ferguson, K. Knox, and J. F. Dillon, Jr., J. Chem. Phys. 39, 890 (1963).

convenient to look at $(2\bar{A}-\bar{E})/2D$. The calculations give various values for this depending on the parameters used but the best calculations, using configuration mixing, give[1] $(2\bar{A}-\bar{E})/2D \approx -150$. This is of the same sign but about twice as large as is observed in ruby. However, for the garnets and emerald, where all the signs are known or fairly well known, experimentally one obtains $+36$ for YAlG, YGaG, and emerald and $+26$ for LuAlG. The difference between these positive values and the negative theoretical value is very disturbing. The theory[1] is designed for Cr³⁺ that sees inversion symmetry (e.g., garnets) while it gives better agreement with the ruby data, where the Cr³⁺ ion does not see inversion symmetry.

Another way to determine experimentally the relation between the ^2E splitting and the $^4A_2$ splitting is to see the effect of stress on both levels when the Cr³⁺ is in a cubic environment. When MgO is grown with Cr³⁺ as an additive, some of the Cr³⁺ ions are found to occupy cubic sites. (The charge compensation is far removed.) Schawlow et al.[30] have measured the R line splitting when the crystal is stressed along a ⟨111⟩ direction. Stress in this direction will cause a deviation from cubic symmetry of the same type as seen in the garnets. Watkins and Feher[31] and Shiren[32] have done a similar experiment, but on the $^4A_2$ state. These measurements[31,32] give values of $2G_{44}[\equiv d(2D)/de$ where e is the strain]. The value for G_{44} is $+4.2$ cm⁻¹/unit strain[31] or $|6.5|$ cm⁻¹/unit strain.[32] For $d(2\bar{A}-\bar{E})/d(2D)$ one finds

$$(de/d(2D))(d(2\bar{A}-\bar{E})/d(-p))(-C_{44})$$
$$= (1/2G_{44})(-2.8\times10^{-10}\ \text{cm/dyn}) \quad (6)$$
$$(-14.99\times10^{11}\ \text{dyn/cm}^2) = +50\ \text{or}\ |35|.$$

These values are in reasonable agreement with the garnets in sign and magnitude. It thus seems clear that a theory that does not consider inversion symmetry must aim to reproduce the garnet or MgO stress results

and not the ruby results at least as far as the ^2E and ^4A state splittings are concerned.

There is one small point about the symmetry of the Cr³⁺ site in emerald. $(2\bar{A}-\bar{E})/2D$ for emerald is about the same as observed for the garnets and MgO under stress. The site symmetry is $32(D_3)$. This means that some, but not necessarily all, of the odd crystal-field terms discussed by Artman and Murphy[3] are zero. For example, the B_1^0 ($\propto \cos\theta$) and B_3^0 ($\propto 5\cos^3\theta-3\cos\theta$) are zero but others are not.[3] Thus the magnitude of the odd crystal field in emerald is possibly very much smaller than in ruby. On the other hand, the agreement between emerald and the stress experiments may be just coincidence. Electric-field-effect experiments could elucidate this point.

The calculations of Artman and Murphy[3] indicate that the previous results on the R-line splitting are not affected to any large extent by the odd terms in the crystal field. However, these odd crystal-field terms will give a contribution to the ground state splitting $(2D)$ which is always negative. Only three samples for which Cr³⁺ does not see inversion symmetry have been measured. D is indeed negative in all three. This small sampling includes ruby, GASH[33], and emerald. For ruby and GASH the site symmetry is $C_3(3)$ but for emerald it is $D_3(32)$ and as discussed in the last paragraph the result for emerald is not clear.

It is apparent, as can easily be seen in Fig. 6, that the ^2E and $^4A_2$ state splittings are not linearly related. The agreement between strained MgO and the garnets suggests that the splittings of these states are linearly related for small deviations from cubic symmetry along the threefold axis of the octahedrally coordinated Cr³⁺. Extending the supposition one could say that at crystal fields large enough to produce positive $2D$ values of approximately $+2$ cm⁻¹ the nonlinear effects are large enough to reduce the R line splitting to small values.

It should be pointed out that results for Cr³⁺ at lower symmetry sites have not been discussed at all because of the lack of theoretical calculations.

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[31] G. D. Watkins and E. Feher, Bull. Am. Phys. Soc. 7, 29 (1962).
[32] N. S. Shiren, Bull. Am. Phys. Soc. 7, 29 (1962). See also N. S. Shiren, Proceedings of the 11th Colloque Ampere, Eindhoven, July 2–7, 1962 (North-Holland Publishing Company, Amsterdam, 1963), p. 114.

[33] J. Overmeyer and G. Burns (unpublished).