

## Optical Absorption in MgO : Cr<sup>3+</sup>

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Experimental measurements of the absorption cross sections of the sharp  ${}^4A_2 \rightarrow {}^2E$  transitions in triply charged chromium ions in MgO are described. The measured *R*-line absorption strength per ion is in good agreement with the value calculated by Macfarlane. Values for the absorption strengths of the *N* lines are obtained and are shown to be consistent with what is known from fluorescence studies about the dipole nature of these transitions. Some sharp lines are seen in absorption which do not appear in fluorescence and the possibility that these are caused by transitions originating on chromium ions in rhombic sites is discussed.

### I. INTRODUCTION

MgO has a very simple lattice which can act as a host for a number of transition-metal ions of optical and ESR interest. Because of this simplicity, MgO:*M*, where *M* is a substitutional impurity ion, would seem to be an ideal system for the study of basic processes in spectroscopy inasmuch as theoretical calculations of crystal field effects should present the least difficulty here. This simplicity was used to advantage by Sugano, Schawlow, and Varsanyi<sup>1</sup> and by Schawlow, Piksis, and Sugano<sup>2</sup> in optical studies of line splitting by magnetic and strain fields, and was also used by Wertz and Auzins,<sup>3</sup> Griffiths and Orton,<sup>4</sup> and later workers<sup>5</sup> in ESR studies. The strong optical fluorescence transition in Cr<sup>3+</sup> in an octahedral (cubic) site in MgO (the "*R* line") was shown by Sugano<sup>1</sup> to be a pure magnetic dipole transition and as such is amenable to fairly accurate calculation of oscillator strength. This calculation was performed by Macfarlane.<sup>6</sup> At about the same time large single crystals of chromium-doped MgO became available and it became possible to measure with accuracy the absorption coefficient per ion. The present work was initially undertaken to supply Macfarlane with *R*-line absorption data for comparison with his calculations. We give here the details of the optical experiments, the method of estimating spins, and some additional observations of the sharp line absorption and fluorescence spectrum.

In this material the triply charged chromium ion substitutes for a doubly charged magnesium ion and the charge discrepancy is compensated for by the occurrence of vacancies in some cation sites. When a vacancy is near a Cr<sup>3+</sup> ion, the symmetry of the crystal field at the chromium site is reduced from cubic to noncubic symmetry and these noncubic ions possess characteristic optical and ESR transitions. The ESR studies show that the non-

cubic chromium sites are mainly of two kinds: One is uniaxial with an axis of symmetry along a [100]-type direction (tetragonal site), and the other is an orthorhombic site, with typical axes [110],  $[\bar{1}\bar{1}0]$ , and [001] (rhombic site).<sup>3,4</sup>

### II. EXPERIMENTAL WORK

The optical absorption experiments were carried out mainly on two large samples (lengths 2.3 and 1.75 cm, respectively). Doping was approximately 0.02 and 0.05% in these samples. A Jarrell-Ash 1-m Ebert spectrometer was used in the initial stages of the work and a Jarrell-Ash 1-m Czerny-Turner spectrometer was used in the later stages. To obtain a continuous visible spectrum suitable for absorption study a quartz-halogen lamp (type DVY) which operates at 650 W with a small filament was found very suitable. To eliminate stray light and the possibility of exciting fluorescence with the absorption light beam the sample was placed at the exit slit of the spectrometer. The absorption measurements were made at liquid-nitrogen temperatures.

To excite fluorescence a high-pressure mercury arc lamp was used. Fluorescence measurements were made at 77° and 2°K.

To measure the concentration of chromium ions in the various sites a small section was taken from each crystal and its ESR spectrum was compared with the spectrum of a CuSO<sub>4</sub> standard sample of known Cu<sup>2+</sup> spin number. A Varian E-3 spectrometer operating at *X* band was used. Cr<sup>3+</sup> is a spin quartet in the ground state, and in the cubic site the three transitions  $\frac{3}{2} \leftrightarrow \frac{1}{2}$ ,  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ , and  $-\frac{1}{2} \leftrightarrow -\frac{3}{2}$  should occur at the same microwave frequency. In the noncubic sites the  $\pm \frac{3}{2}$  and  $\pm \frac{1}{2}$  levels (referred to appropriate axes) are separated from each other and three separate microwave transitions occur for each site. Now it is believed<sup>7</sup> that the sharp ESR signal from cubic Cr<sup>3+</sup> ions is due only to the

$\frac{1}{2} \leftrightarrow -\frac{1}{2}$  transitions, the others being too badly strain broadened to appear. No similar broadening occurs for the noncubic sites. Hence, in using the ESR data to count spins, the cubic ESR signal was attributed only to  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  transitions. The resultant spin count in one sample is given in Table I.

### III. OPTICAL SPECTRUM OF MgO:Cr<sup>3+</sup>

The absorption spectrum in the visible consists of two strong broad bands peaking at 6200 and 4450 Å which correspond, respectively, to  ${}^4A_2(t_2^3) \rightarrow {}^4T_2(t_2^2e)$  and  ${}^4A_2(t_2^3) \rightarrow {}^4T_1(t_2^2e)$  transitions in the chromium ions mainly in cubic sites. A number of sharper but very weak absorption lines, corresponding to  ${}^4A_2(t_2^3) \rightarrow {}^2E(t_2^2)$  transitions on Cr<sup>3+</sup> ions in various sites, are also found.<sup>8,9</sup> These latter transitions will be discussed more fully later. The fluorescence spectrum at 77 °K is shown in Fig. 1, the chromium spin concentration being about 0.05% in this sample. We distinguish two regions of interest. The first is the lower-wavelength region with the sharp lines. The R line at 6981 Å is the  ${}^2E \rightarrow {}^4A_2$  transition of Cr<sup>3+</sup> in the cubic sites and is a purely magnetic dipole transition. The weaker sharp lines in this first region come from Cr<sup>3+</sup> ions in noncubic sites and we refer to them as *N* lines. The pair of lines at 6992 and 7038 Å come from the split  ${}^2E$  level of Cr<sup>3+</sup> ions in tetragonal sites. The 6992-Å line is the weaker because of the Boltzmann factor. The tetragonal distortion is caused by a vacancy in the nearest Mg site in a [100]-type direction and this Cr-vacancy center is illustrated in Fig. 2(a). These optical transitions occur partly by magnetic dipole and partly by electric dipole processes.<sup>9</sup> The lines at 6989 and 7035 Å (including the adjacent small lines at around 7036 Å) are believed to originate on pairs of chromium ions on either side of a vacancy with the Cr-vacancy-Cr axis directed along a [110]-type direction. This center is shown in Fig. 2(b).

The rhombic-site chromium ions which are easily detected by ESR are believed to have a vacancy in the nearest Mg site in a [110]-type direction. This center is illustrated in Fig. 2(c). Glass<sup>10</sup> has suggested that some of the weak sharp fluorescence lines at around 7086 Å could originate on this rhombic center.

TABLE I. Densities of the cubic-, tetragonal-, and rhombic-site Cr<sup>3+</sup> ions in one sample.

Symmetry of chromium site	Number of spins per cm <sup>3</sup>	Percentage of all spins
Cubic	$17.7 \times 10^{18}$	81
Tetragonal	$3.2 \times 10^{18}$	15
Rhombic	$0.85 \times 10^{18}$	4

The second region, from 7100 to 7300 Å, consists of vibronic sidebands of the sharp *R* and *N* lines. It is possible to separate the sidebands associated with the 6981, 7035, and 7038-Å lines, and in the case of each it is found that the sidebands are more intense than the no-phonon lines. It is believed that the sidebands are pure electric dipole transitions (induced by the odd-parity component of the lattice vibrations) and hence appear strong relative to the weaker no-phonon lines.<sup>11</sup>

The new data available from our experiments consist of improved absorption spectra of the sharp *R* and *N* lines. The over-all transmission spectrum in the region of the *R* and *N* lines is shown in Fig. 3, together with fluorescence data, both taken at liquid-nitrogen temperatures. This absorption is discussed further in Sec. IV.

### IV. ANALYSIS OF DATA

#### A. Absorption in *R* Line

We write the transmitted light intensity as

$$I(\omega) = I_0 e^{-k_\omega d}, \quad (1)$$

where *d* is the path length through the sample in cm. The frequency  $\omega$  is measured in units of cm<sup>-1</sup>. The absorption coefficient per ion is

$$\frac{1}{N_c} \int k_\omega d\omega, \quad (2)$$

where  $N_c$  is the number of cubic chromium ions per unit volume and the integration is over the frequency region of the *R* line. The coefficient has the dimensions of cm. Taking values of  $k_\omega$  from our experimental transmission traces and using the value of  $N_c$  obtained by ESR spin count we can estimate the absorption coefficient in the *R* line. In the case of the two large samples the values obtained were  $2.3 \times 10^{-20}$  and  $1.8 \times 10^{-20}$  cm. This result is in very good agreement with the value calculated by Macfarlane<sup>6</sup> ( $2.55 \times 10^{-20}$  cm).

#### B. Absorption in *N* Lines

In the sample which gave the larger of the two values for the *R*-line absorption we also measured the absorption coefficient per tetragonal site Cr<sup>3+</sup> ion in the 6992- and 7038-Å lines. The results are

$$6992 \text{ \AA}: \frac{1}{N_T} \int k_\omega d\omega = 3.2 \times 10^{-20} \text{ cm},$$

$$7038 \text{ \AA}: \frac{1}{N_T} \int k_\omega d\omega = 2.65 \times 10^{-20} \text{ cm},$$

where  $N_T$  is the number of tetragonal-site chromium ions per unit volume. These results indicate that the total transition in the tetragonal Cr<sup>3+</sup> ion is about  $\frac{5}{2}$  times as strong as the analogous transitions in the cubic ion, both measured on the same sample. This is consistent with previously men-

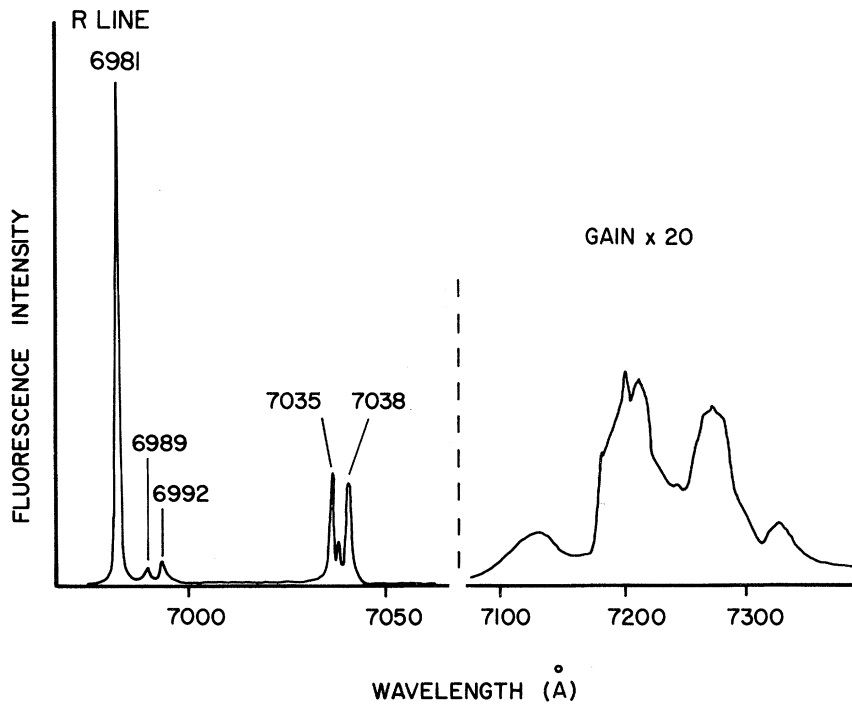


FIG. 1. Fluorescence spectrum of lightly doped  $\text{MgO}:\text{Cr}^{3+}$  at liquid-nitrogen temperature. To show both the broad one-phonon sideband as well as the sharp no-phonon lines on the same figure the gain and wavelength scales are changed in the second part of the spectrum.

tioned analysis of the dipole nature of these  $N$  lines.<sup>9</sup> In that analysis, stress and Zeeman splitting in these lines indicated that this  ${}^4A_2 \leftrightarrow {}^2E$  transition in the tetragonal-site ion occurred by a mixture of electric dipole and magnetic dipole processes—in the ratio 3:2. Since the change in crystal field parameters between cubic and tetragonal sites is small we can assume that the strength of the magnetic dipole process is about the same for the ions in the two sites. Then this 3:2 ratio of electric dipole to magnetic dipole process leads to an expected  $\frac{5}{2}$ -fold increase in strength for the full te-

tragonal-site transition over the cubic  $R$ -line transition, just as we find in the present absorption study. Further, taking sideband intensities into account and assuming that nonradiative processes are negligible, these measured absorption cross

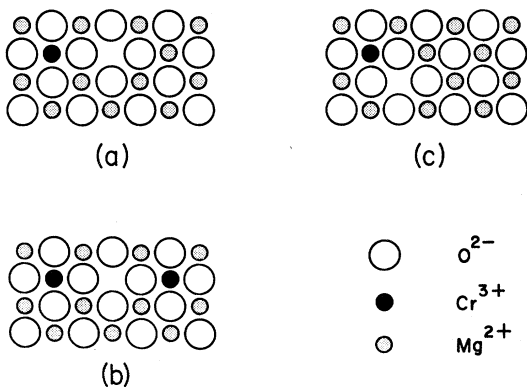


FIG. 2. Representations of the (001) plane of  $\text{MgO}$  showing the environments of  $\text{Cr}^{3+}$  ions in noncubic sites: (a) tetragonal Cr-vacancy center; (b) rhombic Cr-vacancy center; (c) tetragonal Cr-vacancy-Cr center.

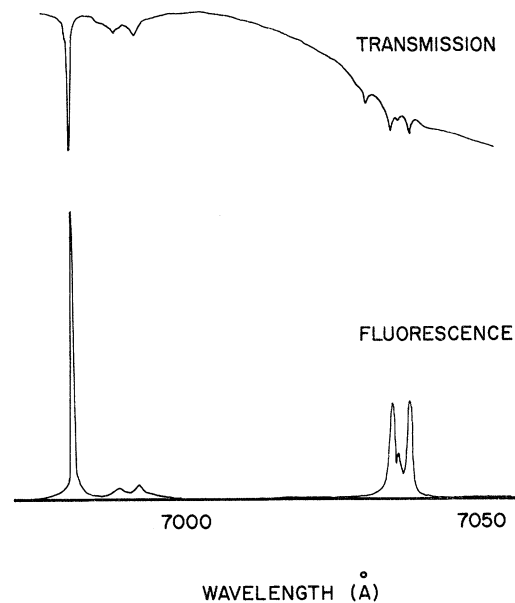


FIG. 3. Transmission and fluorescence traces in the region of the  $R$  and  $N$  lines for the same sample. The temperature is  $77^\circ\text{K}$  and the baseline is the same for both traces.

sections predict a ratio of 5:3 between the radiative decay time of  $R$  and 7038-Å lines.<sup>12</sup> The observed decay times are 11.6 msec for the  $R$  line and 8.6 msec for the 7038-Å line, in reasonable agreement with the present absorption measurements. The consistency of the absorption measurements with both the lifetime data and with the knowledge of the dipole character of the lines can be regarded as an indication that we were correct in our procedure of counting the cubic site spins, that is, in assuming that the cubic ESR line is due only to  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  microwave transitions.

#### C. Fluorescence Strength of the $N$ Lines

As Fig. 3 shows, the main  $N$  lines appear somewhat stronger (relative to the  $R$  line) in fluorescence than in absorption, taking the Boltzmann factor into account. This behavior is not unexpected. First of all we note that the intensity of the sharp line  $\text{Cr}^{3+}$  fluorescence in all materials depends more upon the strength of the band absorption than upon the strength of the fluorescence transition. Further the fluorescence behavior from  $\text{MgO}:\text{Cr}^{3+}$  is complicated by the fact that even at low temperatures some emission occurs from the  ${}^4T_2$  level of  $\text{Cr}^{3+}$  and the fraction which comes out in the  ${}^2E$  level presumably varies among the different kinds of

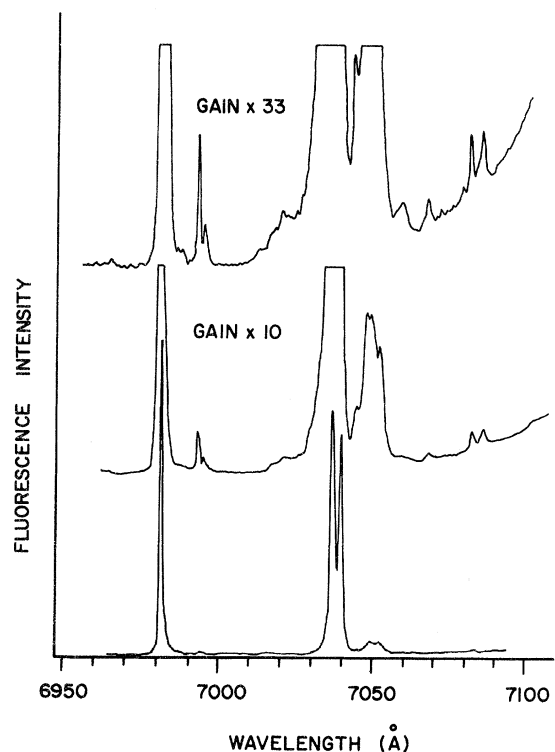


FIG. 4. Fluorescence traces at 2°K. For clarity the baselines of the traces at different gain settings are shifted from one another.

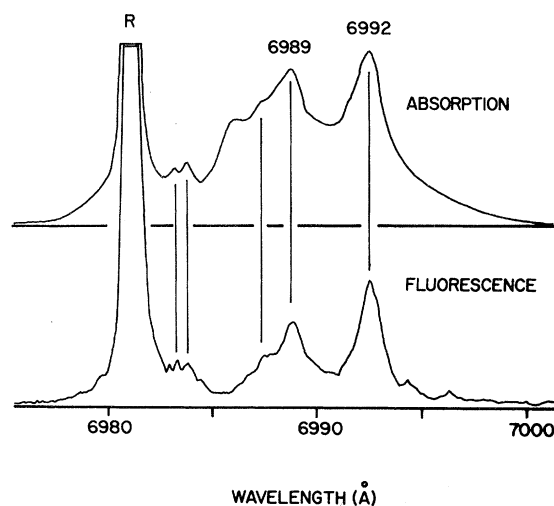


FIG. 5. Comparison of absorption and fluorescence in the same sample at liquid-nitrogen temperature. The region from 6980 to 7000 Å is shown in detail.

site.<sup>13</sup> On the basis of lifetime measurements we can definitely say that the enhancement of  $N$ -line fluorescence is not due to energy transfer from the cubic metastable  ${}^2E$  level.

#### D. Sharp Lines in the 7086-Å Region

This region is of interest since Glass has suggested that the line seen in our crystal at 7086 Å might come from the rhombic Cr-vacancy center, while the line at 7082 Å might come from a rhombic Cr-vacancy-Cr center.<sup>10</sup> Glass made his measurements at 90°K and he gives these wavelengths as 7088 and 7084 Å. We try to check this suggestion by relating the number of rhombic Cr-vacancy centers (as measured by ESR) with the absorption in these lines. Our argument is as follows. We would expect, roughly, the same absorption cross section in the tetragonal and rhombic sites. The concentration of tetragonal sites is four times higher than the concentration of rhombic sites (see Table I) and the linewidth of the rhombic ion transition will be perhaps 50% larger. Based on the strong tetragonal ion transitions obtained with our samples we would expect to see the absorption in the rhombic-site ions with a signal-to-noise ratio of about 4. No absorption was detected in these lines in our samples.

These lines appear in fluorescence in our samples, but they appear very weakly. A fluorescence spectrum taken at 2°K is shown in Fig. 4. (We show a trace taken at helium temperatures since the lines are narrower, the 6989- and 6992-Å lines are reduced to negligible size by thermal depopulation, and as a result the weaker lines are more clearly seen.) The integrated intensity of the

7086-Å line is less than 1% of the 7039-Å intensity in our samples, whereas Glass found in his samples that his 7088-Å lines are about 10% of the 7038-intensity. We feel that the failure to detect a measurable absorption in the 7086 and 7082-Å lines must throw some doubt on the interpretation of these lines as originating on rhombic-site chromium ions.

#### E. Additional Lines Seen in Absorption

As both Figs. 5 and 6 show, some lines are found in absorption which do not occur in fluorescence. For example, the lines at 7031 and 7042 Å, which are about as strong in absorption as the strongest *N* lines, do not appear in fluorescence. There would also appear to be some additional structure in absorption at around 6988 Å, and these are seen in all the large samples we studied. They could be due to Cr-vacancy-*M* centers, where *M* is any one of a number of impurity ions which occur in MgO. Such centers are found in ESR work. We consider the possibility that these additional absorption lines (rather than the 7082- and 7086-Å fluorescence lines) are transitions on the rhombic site  $\text{Cr}^{3+}$  ions. We would expect that the very close vacancy in the rhombic center would lead to large splitting and broadening,<sup>14</sup> and to large admixture of odd crystal field and hence strong optical transitions. The positions, widths, and strengths of these additional lines agree with these predictions. The greater strain sensitivity of the rhombic-site ions could cause the emission from these centers to occur mainly from the  ${}^4T_2$  levels, hence the  ${}^2E \rightarrow {}^4A_2$  transitions would not appear strongly in fluorescence. This could account for the experimental fact that these additional transitions do not appear in fluorescence.

#### F. Conclusion

The absorption strength in the *R* line which is measured here with good accuracy afforded an important check on Macfarlane's theoretical estimations of magnetic dipole optical processes. The measured absorption strength of the tetragonal-

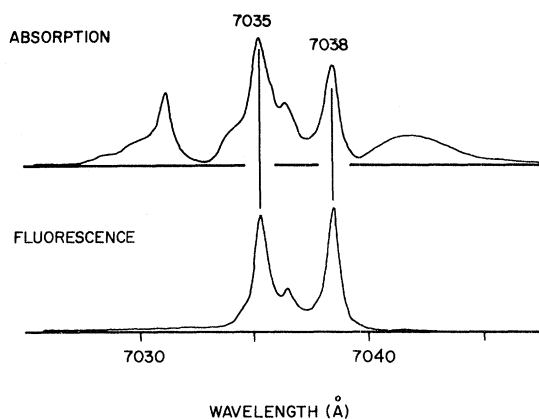


FIG. 6. Comparison of absorption and fluorescence in the same sample at liquid-nitrogen temperature. The region from 7025 to 7045 Å is shown in detail.

site *N* lines is consistent with what is known of the dipole nature of these lines. The lack of detectable absorption in the 7086-Å region questions the interpretation of the lines in that region as originating on rhombic-site chromium ions. Some new lines appear on absorption which must also be regarded as candidates for rhombic ion transitions.

#### ACKNOWLEDGMENTS

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<sup>1</sup>S. Sugano, A. L. Schawlow, and F. Varsanyi, *Phys. Rev.* **120**, 2045 (1960).

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

<sup>3</sup>J. E. Wertz and P. Auzins, *Phys. Rev.* **106**, 484 (1957).

<sup>4</sup>J. H. E. Griffiths and J. W. Orton, *Proc. Phys. Soc. (London)* **73**, 948 (1959).

<sup>5</sup>For a review, see B. Henderson and J. E. Wertz, *Advan. Phys.* **17**, 749 (1968).

<sup>6</sup>R. M. Macfarlane, *Phys. Rev. B* **1**, 989 (1970).

<sup>7</sup>The  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  transition is sharper than the other ESR transitions, such as  $\frac{1}{2} \leftrightarrow \frac{3}{2}$ , in the ESR spectra of  $\text{Cr}^{3+}$ ,

$\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  [E. R. Feher, *Phys. Rev.* **136**, A145 (1964)]. This is due to random strains which, for example, in the case of  $\text{Cr}^{3+}$ , can split the position of the  $\pm\frac{1}{2}$  levels from that of the  $\pm\frac{3}{2}$  levels and which, as a result broadens the  $\frac{1}{2} \leftrightarrow \frac{3}{2}$  transitions. The  $\pm\frac{1}{2}$  levels are unsplit by such strains, hence the  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  transition is unaffected by such strains and stays sharp.

<sup>8</sup>A. L. Schawlow, *J. Appl. Phys.* **33**, 395 (1962).

<sup>9</sup>G. F. Imbusch, A. L. Schawlow, A. D. May, and S. Sugano, *Phys. Rev.* **140**, A830 (1965).

<sup>10</sup>A. M. Glass, *J. Chem. Phys.* **46**, 2080 (1967).

<sup>11</sup>G. F. Imbusch, *Microwave Laboratory Rept. No.* 1190, Stanford University, 1964 (unpublished).

<sup>12</sup>The intensity ratio of the  $R$  line to its sideband is about 1:2.5 at 77 °K. Neglecting nonradiative processes the total decay rate from the  ${}^2E$  level is then 3.5 times as strong as the  $R$ -line radiative process. We also estimate in a similar manner that the total decay rate from the  ${}^2E$  level of the tetragonal site is 2.4 times as strong as the  $N$ -line (6992 and 7038 Å) radiative process. From the measured 5:2 ratio between the transition strengths of the  $N$  and  $R$  lines we expect that the ratio of the decay rates from the  ${}^2E$  levels of the cubic and tetragonal sites

is  $\frac{2}{5} \times 3.5/2.4 \approx \frac{3}{5}$ , and the expected ratio of decay times is therefore 5:3.

<sup>13</sup>J. H. Parker, R. W. Weinert, and J. C. Castle, in *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Wiley, New York, 1967), p. 251.

<sup>14</sup>There is a ground-state splitting of  $0.8 \text{ cm}^{-1}$  in the rhombic site as measured by ESR. This would cause a broadening of the optical line on this site.

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## Tetragonal-Field Splittings of Levels in $\text{MgO}:\text{Cr}^{3+}$ †

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Detailed ground-state and selective-excitation traces reveal new  ${}^2T_1$  and  ${}^2T_2$  levels in  $\text{MgO}:\text{Cr}^{3+}$ . Computer diagonalizations are carried out to confirm the identity of the absorbing system. Detailed perturbation-loop calculations, which agree with results of the diagonalization, help to determine the causes of level splittings. Improved tetragonal-field parameters are given. The  ${}^2T_2$  levels are assigned to the vacancy or pair-vacancy systems, whereas the  ${}^2T_1$  levels are assigned to the cubic system. Assignment of other features to the  ${}^2T_1$  levels of the vacancy system is tentative.

### I. INTRODUCTION

When trivalent  $\text{Cr}^{3+}$  is substituted for divalent  $\text{Mg}^{2+}$  in a cubic  $\text{MgO}$  crystal, two  $\text{Cr}^{3+}$  ions and one vacant site replace three  $\text{Mg}^{2+}$  ions. Many  $\text{Cr}^{3+}$  ions enter purely cubic sites where there is no local charge compensation. Others (at most, 50%) enter sites with a vacancy in the [001] direction (tetragonal) and to a much lesser degree the [011] direction (rhombic).<sup>1</sup> In more strongly doped samples a "pair-vacancy" system of two  $\text{Cr}^{3+}$  ions adjacent to a vacancy is observed.

In absorption and fluorescence measurements the effects of the different systems sometimes overlap. However, by varying stress and concentration, the  $R$  line and sideband fluorescence of the cubic, tetragonal vacancy, and tetragonal pair-vacancy systems, have been separated.<sup>2-5</sup> Macfarlane analyzed the observed splittings of the  $(t_2^3) {}^2E$  and  ${}^4A_2$  levels in the vacancy system by perturbation-loop calculations for a weak tetragonal field.<sup>6</sup> Recent excited-state-absorption measurements have found two new sharp-line levels,  ${}^2T_2(t_2^3)$  and  ${}^2A_2(t_2^2 e)$ , which required identification of the absorbing system.<sup>7</sup> Two new sharp lines in the expected region of the  $B$  lines ( ${}^4A_2 \rightarrow {}^2T_2$ ) were found in the course of careful ground-state measurements needed to correct the excited-state-absorption data.<sup>7</sup> Intensity calculations were consistent with assigning all these new sharp-line transitions to the vacancy and pair-vacancy systems of tetragonal symmetry.

This paper, therefore, presents further analysis and system identification of the sharp-line transitions in  $\text{MgO}:\text{Cr}^{3+}$ . Detailed measurements of ground-state absorption determine the splitting of the  ${}^2T_2$  level and the antiresonance parameters of interaction with the  ${}^4T_1$  band. A new pair of  ${}^2T_1$  levels seen photographically by Imbusch but not identified by him<sup>4</sup> is resolved in detail. The systems responsible for these lines are then identified by selective-excitation measurements which separate the ground-state-absorption contributions of the various systems. From the new experimental data better tetragonal-field parameters are found for the vacancy and pair-vacancy systems. Extended perturbation-loop calculations and diagonalization of the energy matrices with these parameters give a good fit to all observed levels.

### II. EXPERIMENTAL

Ground-state-absorption measurements were made at low temperatures on three  $\text{MgO}:\text{Cr}^{3+}$  crystals of different concentrations varying from light yellow to dark green.<sup>8</sup> Samples No. 1 and 3 were mounted in the sample chamber of a Cary 14 spectrometer in the same double-walled glass Dewar used in excited-state-absorption measurements.<sup>7</sup> Cold nitrogen gas flowed through the Dewar to cool the crystals to approximately 100 °K. The rest of the sample chamber and the interior of the Cary were filled with warm dry nitrogen gas to prevent frosting. The lightly doped sample No. 2