Fluorescence of MgO:Cr^{3+} Ions in Noncubic Sites*

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In addition to the R line at 6981 Å, the fluorescence spectrum of MgO:Cr^{3+} contains a number of sharp lines in the region between 6981 and 7040 Å. The strongest of these are identified, by their splitting under axial stress, with ions in sites of tetragonal symmetry. Such tetragonal symmetry at the ion site can be produced by an adjacent magnesium-ion vacancy. The vacancy also produces some hemihedral field at the chromium ion, and so the transitions from these chromium ions need not be purely magnetic-dipole. They are found to have also some electric-dipole character. Lines from pairs of chromium ions, with a small exchange interaction, are also identified.

INTRODUCTION

WHEN Cr^{3+} is substituted for Mg^{2+} in a weakly doped sample of MgO:Cr^{3+}, most of the chromium ions enter sites of octahedral (cubic) symmetry. Absorption can occur from the $^4A_{2g}$ ground state to all the excited states, but the ions relax rapidly to the metastable ^2E_g state and the only fluorescence is between ^2E_g and $^4A_{2g}$. In a purely cubic field these levels are unsplit and the ion emits a single sharp line at 6981 Å (R line).

To the red of the R line, the fluorescence spectrum contains a number of other sharp lines[1] within a few hundred cm^{-1}. Unlike ruby, most of these lines do not disappear at low chromium concentrations. They can, therefore, not be attributed to pairs of chromium ions alone, but are more likely to arise from ions in noncubic sites.[2,3]

When a Cr^{3+} ion is substituted for a Mg^{2+} ion in MgO, a charge discrepancy is introduced since a trivalent ion replaces a divalent one. This discrepancy is compensated for by the occurrence of vacancies in some magnesium sites. For every two Cr^{3+} ions introduced, one Mg^{2+} vacancy occurs. Thus, some chromium ions find a vacancy in an adjacent lattice site which disturbs the cubic environment and lowers the chromium site symmetry. The ^2E_g and $^4A_{2g}$ levels of such ions are split by this disturbance. This is similar to the situation in ruby where an internal trigonal field lowers the site symmetry from cubic.

The ground-state splitting of Cr^{3+} ions in noncubic sites in MgO has been investigated by Wertz and Auzins,[4] and by Griffiths and Orton,[5] using paramagnetic-resonance techniques. They found that in the case of ions with a noncubic component of the field in the [100] direction (tetragonal field) the ground state was split by 0.16 cm^{-1}. On the other hand, the ground-state splitting for Cr^{3+} ions in a rhombic field (noncubic component in the [110] direction) was found to be 0.8 cm^{-1}. They suggested that the departure from cubic symmetry in these cases was due to the Mg^{2+} vacancies in the [100] and [110] directions. Although there is little *direct* spectroscopic or ESR evidence to support this view we will continue to describe the noncubic sites in terms of a vacancy combined with one or more Cr^{3+} ions.

The sharp optical lines emitted by the chromium ions in noncubic sites are found to the red of the R line, and they occur in two groups: at around 6990 and 7038 Å. They are called satellite lines, or N lines (from the German *Nebenlinien*).[1] These groups are shown in Figs. 1 and 2, and some of the lines are seen to be strongly concentration-dependent.

At very weak doping (less than a hundred chromium ions per million magnesium ions) the strongest of these N lines consists of a pair at 6992 and 7038 Å. These wavelength values are probably only correct to within 1 Å and should be regarded as labels rather than accurate absolute values of the wavelengths of these lines. The exact wavelengths vary slightly depending on the method of preparation of the crystal. The relative intensity of the 6992- and 7038-Å lines varies with temperature roughly in the same way as the Boltzmann factor between 20° and 90°K, and so these lines would appear to be emitted by the split ^2E_g level of a chromium-vacancy system. Since the line width of the 7038-Å line of a moderately doped crystal is around 0.3–0.4 cm^{-1}, which is less than the 0.8 cm^{-1} ground-state splitting of the chromium ion with a vacancy in the

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[1] O. Deutschbein, Ann. Phys. Ser. 5, **14**, 712 (1932).

[2] A. L. Schawlow, D. L. Wood, and A. M. Clogston, Phys. Rev. Letters **3**, 544 (1959).

[3] A. L. Schawlow, J. Appl. Phys., Suppl. **33**, 395–398 (1962).

[4] J. E. Wertz and P. Auzins, Phys. Rev. **106**, 484 (1957).

[5] J. H. E. Griffiths and J. W. Orton, Proc. Phys. Soc. (London) **73**, 948 (1959).

[110] direction, the 6992- and 7038-Å lines are suspected to come from the chromium ions with vacancies along the fourfold symmetry axes.[3] The ground-state splitting cannot be resolved optically, but at 4°K the 7038-Å line is broader than the R line by an amount which is consistent with a ground-state splitting of 0.16 cm^{-1}.

As the concentration of chromium ions increases, the lines at 6992 and 7038 Å increase in intensity relative to the R line, as is expected since the probability of a chromium ion and a vacancy being found close together increases with concentration. However, two additional lines, at approximately 6989 and 7034 Å, which are very weak at low concentrations, experience a much larger increase in their intensities (relative to the R line) with concentration. At very heavy concentration (around 0.5% Cr_2O_3) the 7034-Å line is stronger than the 7038-Å line and is sometimes found to be more intense than the R line. This suggests that the 7034-Å line may be produced by pairs of chromium ions, perhaps in conjunction with a magnesium vacancy or other charge-compensating defect.

The R line of MgO:Cr^{3+} emitted by ions in cubic sites is a magnetic dipole transition.[6] Any perturbation which lowers the site symmetry from cubic causes the E_g level to split in two, with a corresponding splitting[2] of the R line. If the perturbation is of even symmetry

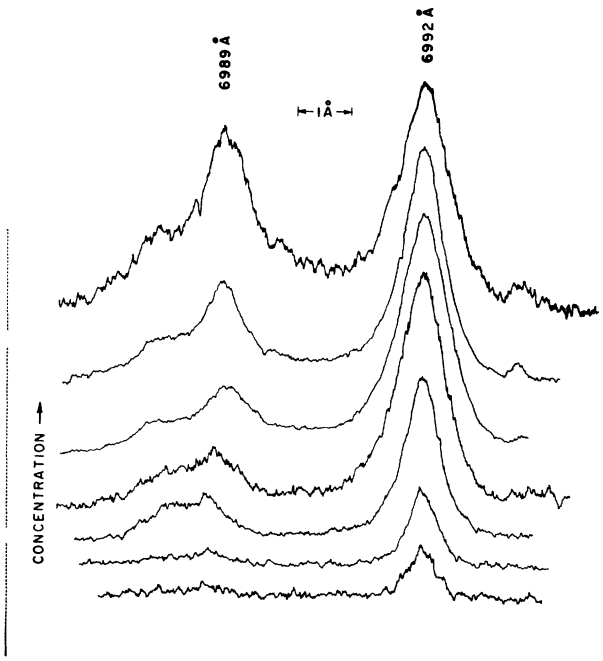

FIG. 1. Relative intensities of the fluorescence lines at 6990 Å as a function of chromium concentration. The measurements were made at 77°K. The concentrations range from a few chromium ions per million magnesium ions (lowest trace) to around 0.2% Cr_2O_3 (upper trace).

[6] S. Sugano, A. L. Schawlow, and F. Varsanyi, Phys. Rev. **120**, 2045 (1960).

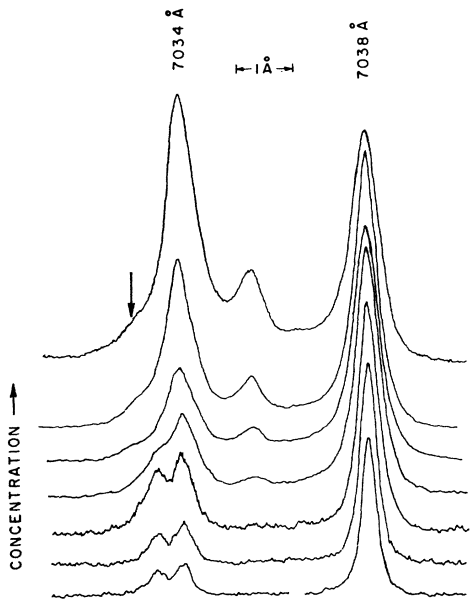

FIG. 2. Relative intensities of the fluorescence lines at 7038 Å as from the same samples as those in Fig. 1. The measurements were made at 77°K.

the parity-forbidden selection rule still holds and the transition remains a magnetic-dipole process. Such even perturbations can be introduced by applying external strains on the crystal.[7]

The N lines of MgO:Cr^{3+} are believed to come from chromium ions in crystal sites whose symmetry is reduced from cubic by the presence of a nearby vacancy. The nearby vacancy can be considered to introduce an internal strain at the environment of such a chromium ion. The ^2E_g level of each such ion is split in two and two R lines are emitted. The vacancy, however, also introduces a perturbation of odd symmetry which relaxes the parity-forbidden selection rule and allows some electric-dipole radiation in the fluorescence from these chromium ions. If the odd perturbation is sufficiently large, a detectable amount of electric-dipole radiation may occur in these N lines.

We have investigated these N lines to find out what type of chromium-vacancy system emits them and whether their radiation is magnetic-dipole (mag. dip.) or electric-dipole (elec. dip.).

METHOD OF INVESTIGATION

The symmetry of the chromium-vacancy system which emits the 6992- and 7038-Å lines was investigated by the Kaplyanskii method[8] of applying uniaxial pressures to the crystal and observing the splitting of the lines.

The effect of uniaxial pressures on the R line emitted

[7] A. L. Schawlow, A. Piksis, and S. Sugano, Phys. Rev. **122**, 1469 (1961).

[8] A. A. Kaplyanskii, Opt. Spectr. (USSR) **7**, 406, 409 (1959).

by the ion in a cubic site has been investigated by Schawlow, Piksis, and Sugano.[7] The application of a uniaxial pressure reduces the site symmetry from cubic, the ^2E_g level splits in two, and the center of gravity of the level also moves. Thus, the R line splits in two and its center shifts to the red with increasing pressure.

The effect of pressure on the 6992- and 7038-Å lines is different from its effect on the R line. The ^2E_g level of the chromium ion which emits these lines is already split into two Kramers doublets by the vacancy and no further splitting can be introduced. The lines can, however, shift under the stress. Consider the chromium ions with a nearby vacancy along a fourfold symmetry axis. There is equal probability that the vacancy is situated along either the [100], [010], or [001] directions. An uniaxial stress applied along [001] will affect the chromium-vacancy system which is oriented along [001] in a different manner to the systems oriented at right angles to the stress. Both of these systems will have their individual spectral lines shifted by different amounts, and the N lines from all these ions will appear to split up under uniaxial pressure along [001].

If such a stress is applied along the [111] direction, the chromium-vacancy systems oriented along the [100], [010], and [001] directions undergo the same type of strain, the lines shift by the same amount and no apparent splitting occurs. Lines from chromium-vacancy systems oriented along any other directions will split up under such a stress. Experimentally it is found that when pressure is applied along [111], the 6992-, 7034-, and 7038-Å lines shift but do not split. On the other hand, pressure along [001] causes these lines to split. This indicates that the chromium-vacancy systems emitting these lines are oriented along fourfold symmetry axes.

The dipole nature of the radiation at 6992 and 7038 Å was investigated using the following three tests:

(a) The relative intensities of the 6992- and 7038-Å lines can be calculated on the assumption that the transition is (i) magnetic-dipole, and (ii) electric-dipole induced by the odd-parity perturbation introduced by the vacancy. The theoretical predictions can be compared with experiment.

(b) When pressure is applied externally along the [001] direction the lines split up. The pattern of components predicted for magnetic- and electric-dipole transitions can be compared with that observed.

(c) The Zeeman pattern predicted for magnetic and electric-dipole transitions can be compared with the experimental Zeeman patterns.

The results of these tests show that the radiation from the chromium-vacancy systems oriented along the fourfold symmetry axes is mainly magnetic-dipole but that a detectable amount of electric-dipole radiation occurs.

EXPERIMENTAL

Light green crystals of MgO containing about 0.05% chromium were used in the stress and Zeeman experiments. These experiments were carried out at liquid-nitrogen temperature. Crystals whose concentrations ranged from transparent, nominally undoped MgO, to dark green samples were used in measuring the intensities of the 6992- and 7038-Å lines. The crystals were placed in front of a Jarrell-Ash 1.8-m Ebert-Fastie recording spectrometer, and an E.M.I. 9558 or a liquid-nitrogen-cooled R.C.A. 7102 photomultiplier was used as a detector. Fluorescence was excited by illuminating the crystal with light from tungsten filament lamps or from a mercury arc lamp. The exciting radiation was passed through a layer of copper sulfate solution which allowed only blue-green light to fall on the crystal. A red filter was placed before the slit of the spectrometer to allow only the red fluorescence to reach the detector.

To measure the intensities of the 6992- and 7038-Å lines, the response of the spectrometer and photomultiplier was calibrated in the region of interest and the area under the lines was integrated. Measurements were made on a number of crystals at 77° and 90°K. Allowance was made for the Boltzmann factor, and then the relative strengths of the two transitions was obtained from the data. In the case of concentrated samples, it was found that the temperature of the crystal was higher than that of the bath by 2–3° because of the pumping light, and so a correction was made for this fact. The experimental value of the ratio of the strength of the 6992- and 7038-Å transitions was 1.3 ± 0.1.

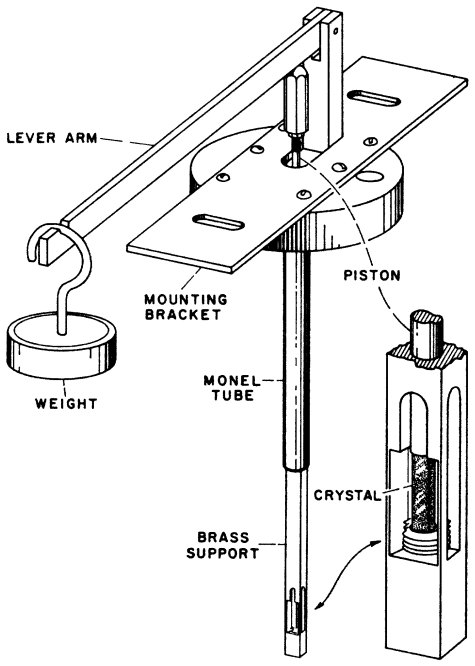

FIG. 3. Apparatus used to apply uniaxial stress to the crystal.

The apparatus used for the pressure experiments is shown in Fig. 3. The crystal was cut into a rectangular prism approximately 10 mm×2 mm×2 mm oriented along the appropriate crystal direction. The prism was mounted in the apparatus and subjected to forces up to 150 kg by means of the piston, lever arm, and weights. The lower part of the apparatus was immersed in liquid nitrogen. When pressure was applied along the [111] direction the 6992- and 7038-Å lines did not split, but they did split under pressure along [001] and the resultant patterns are shown in Figs. 4 and 5.

A magnetic field of around 15,000 Oe was applied along the [001] and [111] crystal directions. The crystals were sliced along the (001) and (111) planes for this experiment and placed between the pole pieces of the magnet. The fluorescence was focused by a lens system onto the slits of the spectrometer. The Zeeman patterns are shown in Figs. 6–9. Crystals of different concentrations were used in the $H_0\|[001]$ and $H_0\|[111]$ experiments, hence, the difference in the ratio of 7034- and 7035-Å intensities in Figs. 6 and 8. A similar difference is seen in the ratio of the 6989- and 6992-Å intensities in Figs. 7 and 9.

THEORETICAL

In the absence of internal or external perturbations, the Cr^{3+} ion occupies a site of octahedral (cubic) symmetry. The eigenfunctions for each energy level span a vector space which belongs to an irreducible representation of the cubic group. The coordinate axes are chosen to lie along the fourfold symmetry axes and the eigenfunctions are defined with respect to these axes.[9] We will be considering perturbations directed along a fourfold symmetry axis which reduce the site symmetry

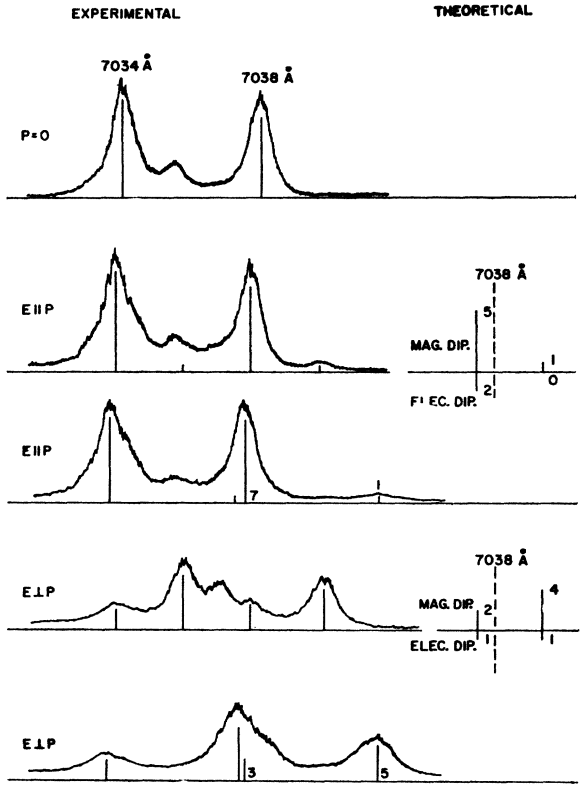

FIG. 4. Splitting of the 7038- and 7034-Å lines under pressure along [001]. Pressures are 23 and 45 kg/mm².

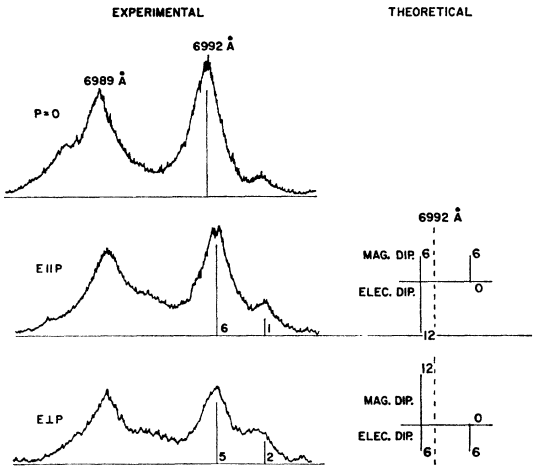

FIG. 5. Splitting of the 6992-Å line under pressure along [001].

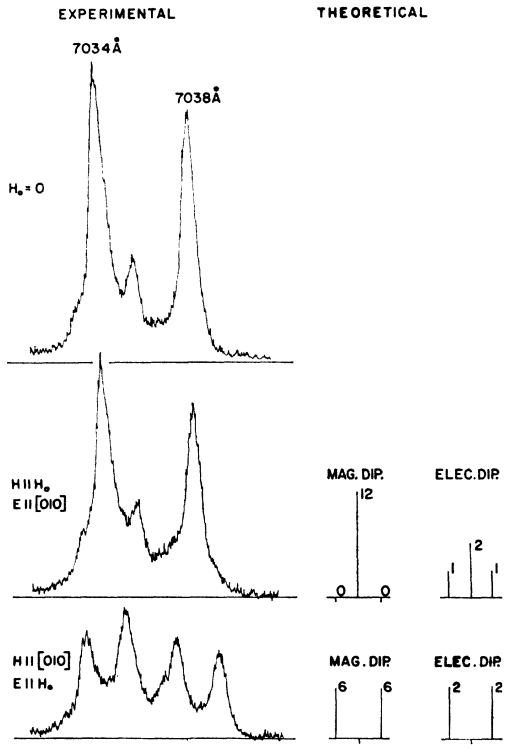

FIG. 6. Zeeman splitting of the 7038- and 7034-Å lines, $H_0\|[001]$. The theoretical splitting for 7038 Å is also shown.

[9] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 753 (1954).

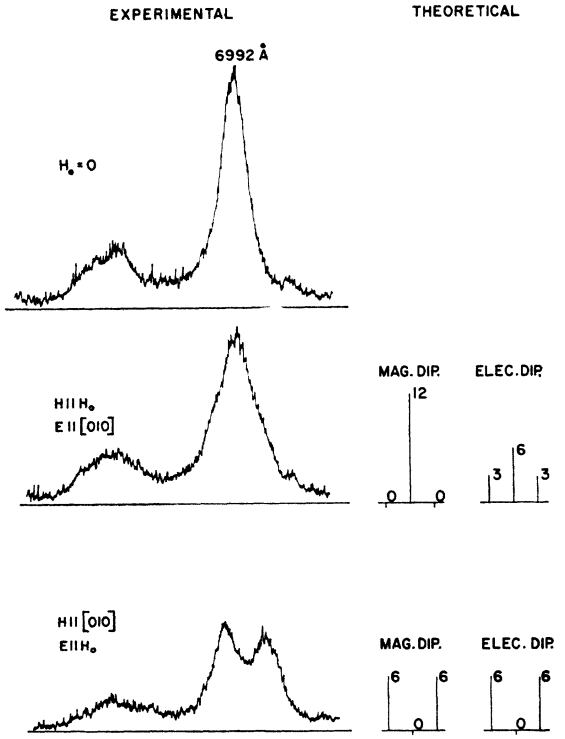

FIG. 7. Zeeman splitting of the 6922-Å line, $H_0 \| [001]$. The theoretical splitting is also shown.

from cubic to tetragonal. It is convenient, then, to choose basis functions for the cubic energy levels which also span spaces belonging to the irreducible representations of the tetragonal group. Such functions are defined in Ref. 9.

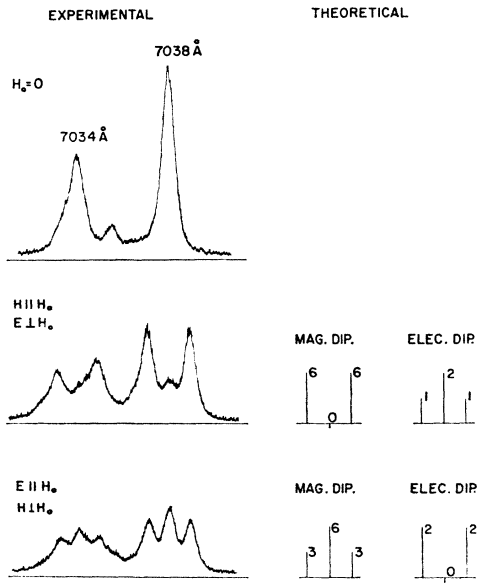

FIG. 8. Zeeman splitting of the 7038- and 7034-Å lines, $H_0 \| [111]$. Theoretical splittings are also shown.

When a vacancy occurs in a direction along one of the fourfold symmetry axes, the environment undergoes an internal strain and the chromium site symmetry is lowered from cubic to tetragonal. It is presumed that the vacancy occurs in a next-to-nearest neighbor position from the chromium ion. It is not intuitively obvious whether the internal strain caused by this vacancy is compressive or extensive. A vacancy in a nearby position might be expected, mechanically, to permit the ions to adjust themselves to fill this vacancy and thereby cause an extensive strain. On the other hand, a charge vacancy upsets the electrostatic balance and the negatively charged oxygen ion, between the chromium ion and the vacancy, might be expected to be pulled in toward the chromium ion. This would cause a compressive strain. Experimentally we can decide what type of internal strain exists by observing how the levels shift and split under pressure along [001]. The experiments indicate that the internal strain is compressive.

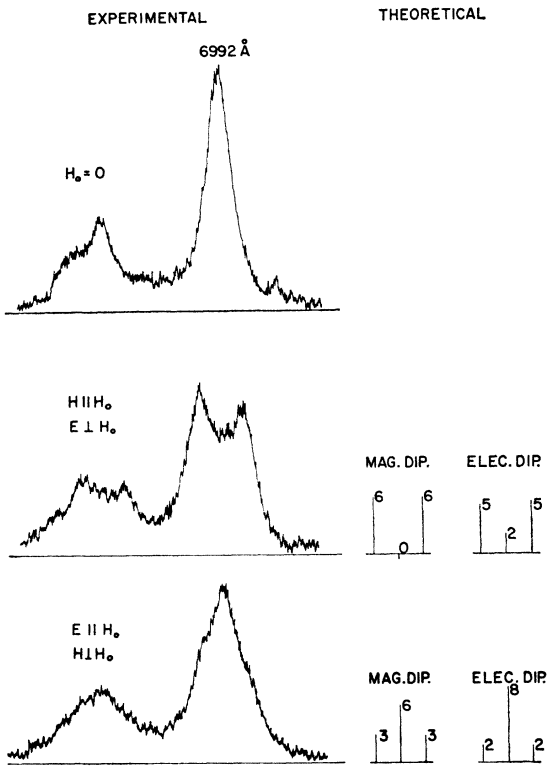

FIG. 9. Zeeman splitting of the 6992-Å line, $H_0 \| [111]$. The theoretical splitting is also shown.

Consider a chromium ion with such a vacancy along the z axis. The internal strain acting on the chromium ion consists of a tetragonal compression which causes a splitting, and a volume compression which causes a shift in the center of gravity of the split components. Only the even-parity tetragonal perturbation is taken

TABLE I. Dependence of excited orbital on polarization of **H**.

Polarization of **H**	Excited $^4T_{2g}$ orbital
x	ξ
y	η
z	ζ

TABLE II. Spin-orbit matrix elements, $\sum_{\bar{M}_s, M_s}|\langle {}^2E_g\phi\bar{M}_s|V_{so}|{}^4T_{2g}\phi' M_s\rangle|^2$.

${}^2E_g\,\phi$ \ ${}^4T_{2g}\,\phi'$	ξ	η	ζ
u	$4(\zeta')^2/3$	$4(\zeta')^2/3$	0
v	$4(\zeta')^2/9$	$4(\zeta')^2/9$	$16(\zeta')^2/9$

into account here when considering the splitting into two of the ^2E_g level. The odd-parity perturbation does not cause any additional splitting of these two levels, but it may be instrumental in inducing electric-dipole transitions. The even tetragonal perturbation separates the two orbital states, ^2E_gu and ^2E_gv, and the u level lies higher than the v level. The $^4A_{2g}$ level also splits up, but by an amount which is so small as to be not optically observable. It facilitates calculations to disregard this small ground-state splitting. The 6992- and 7038-Å lines are emitted by the ^2E_gu and ^2E_gv states, respectively.

If an external uniaxial compression is also applied along the z direction, the tetragonal strain increases and hence the energy-level separation increases. If this external uniaxial compression is applied along the x or y directions no additional splitting occurs. In that case the most significant effect is a lowering of the tetragonal strain and hence a decrease in the separation between the u and v levels.

We consider now the radiation emitted by such a chromium-vacancy system. The matrix element for the magnetic-dipole transition between $|{}^2E_g\phi\bar{M}_s\rangle$ and $|{}^4A_{2g}e_2M_s\rangle$ is[6]

$$\frac{\langle {}^2E_g\phi\bar{M}_s|V_{so}|{}^4T_{2g}\phi' M_s\rangle\langle {}^4T_{2g}\phi' M_s|\mathbf{M}|{}^4A_{2g}e_2M_s\rangle}{W({}^2E_g)-W({}^4T_{2g})}. \quad (1)$$

The square of this matrix element is a measure of the strength of the transition. The $^4A_{2g}$ level is an orbital singlet and its orbital is denoted by e_2. ϕ and ϕ' denote particular orbitals of the ^2E_g and $^4T_{2g}$ levels, respectively. $\bar{M}_s$ and M_s are the z components of spin angular momentum for the ^2E_g and $^4A_{2g}$ levels, respectively, and **M** is the magnetic-dipole-moment operator: $\mathbf{M}=\Sigma_i(\mathbf{l}_i+2\mathbf{s}_i)$. The direction of the magnetic-dipole vector (**H**) of the radiation is parallel to the direction of **M**.

For a given direction of polarization **H**, a certain orbital of the intermediate $^4T_{2g}$ state occurs in Eq. (1). This can be found from the tables of Wigner coefficients for a cubic group.[9] The particular orbitals excited under various directions of polarization are shown in Table I. The absolute value of the Wigner coefficients for all these cases is the same, and its value is not given in Table I.

The spin-orbit matrix elements must now be evaluated. These have been tabulated by Sugano.[6] By knowing which $^4T_{2g}$ orbitals are excited for a given polarization, and by using the spin-orbit matrix elements, the relative strengths of the magnetic-dipole transitions between $|{}^2E_g\phi\bar{M}_s\rangle$ states and the $|{}^4A_{2g}e_2M_s\rangle$ ground states are easily calculated. In the absence of a magnetic field, the $\bar{M}_s$ levels of the ^2E_g states are degenerate, as are the M_s levels of $^4A_{2g}$. In evaluating the strengths of the transitions, then, only values of

$$\sum_{\bar{M}_s, M_s}|\langle {}^2E_g\phi\bar{M}_s|V_{so}|{}^4T_{2g}\phi' M_s\rangle|^2$$

are needed. These are given in Table II. In Table II, ζ' is the value of the spin-orbit matrix element between one-electron states:

$$\zeta'=-\sqrt{2}\langle t_{2g}x_{+\frac{1}{2}}|V_{so}|e_gu_{+\frac{1}{2}}\rangle,$$

where x_+ and u_+ are trigonal basis functions of the T_{2g} and E_g representations, respectively.

Because of the perturbation, V_{odd}, introduced by the vacancy, an electric-dipole transition can occur and its matrix element is given by[6]

$$\sum_{\phi'}\frac{\langle {}^2E_g\phi\bar{M}_s|V_{so}|{}^4T_{2g}\phi' M_s\rangle\langle {}^4T_{2g}\phi' M_s|\tilde{P}|{}^4A_{2g}e_2M_s\rangle}{W({}^2E_g)-W({}^4T_{2g})}, \quad (2)$$

where $\langle {}^4T_{2g}\phi' M_s|\tilde{P}|{}^4A_{2g}e_2M_s\rangle$ is given by

$$\sum_{\Gamma_u\phi''}\frac{\langle {}^4T_{2g}\phi' M_s|\mathbf{P}|{}^4\Gamma_u\phi'' M_s\rangle\langle {}^4\Gamma_u\phi'' M_s|V_{odd}|{}^4A_{2g}e_2M_s\rangle}{W({}^4\Gamma_u)-W({}^4A_{2g})}$$
$$+\sum_{\Gamma_u'\phi'''}\frac{\langle {}^4T_{2g}\phi' M_s|V_{odd}|{}^4\Gamma_u'\phi''' M_s\rangle\langle {}^4\Gamma_u'\phi''' M_s|\mathbf{P}|{}^4A_{2g}e_2M_s\rangle}{W({}^2E_g)-W({}^4\Gamma_u')}. \quad (3)$$

P is the electric-dipole operator, Γ_u and Γ_u' denote states of odd parity, and ϕ'' and ϕ''' are the orbitals of the Γ_u and Γ_u' states, respectively. The direction of the electric-dipole vector (**E**) of the radiation is parallel to the direction of **P**.

Odd perturbations on the chromium ion and its sur-

roundings are of type T_{1u} and E_u. When directed along the z direction these perturbations are functions of type $T_{1u}\gamma$ and $E_u u$. The perturbation T_{1u} enters in the first order and E_u enters in the fifth order in the power expansion with respect to the electron coordinate r. We therefore assume that the effect of E_u is very small and we neglect it in the following arguments. For a given direction of polarization **E**, and under a given odd perturbation, a certain orbital of the $^4T_{2g}$ intermediate state is excited. This orbital can be found from Eq. (3) using the tables of Wigner coefficients, and the information is gathered in Table III. Once again the nonzero Wigner coefficients have the same absolute values. Only an odd perturbation along the z direction, $T_{1u}\gamma$, is considered in Table III. From Tables II and III the relative strengths of the various electric-dipole transitions from a chromium ion with a vacancy along the z direction, can be calculated.

The vacancy which lowers the site symmetry has equal probability of being found along each of the fourfold symmetry axes. It is necessary, then, when considering the radiation emitted by such ions, to consider one representative ion-vacancy system pointing along each of the x, y, and z axes, and sum the radiation from all three. The three representative systems are shown in Fig. 10 and are labeled: (X), (Y), and (Z).

Because of the symmetry of the situation in the absence of external perturbations, the total radiation is isotropic. To calculate the strengths of the transitions, one needs to consider one direction of observation and one polarization. We consider radiation emitted in the x direction with electric vector along z and magnetic vector along y.

Magnetic-dipole transitions are evaluated as follows: Consider the (Z) system. The strain is along the z direction, the u and v orbitals of the ^2E_g state are separated, and the u level is highest. From Tables I and II the transitions from u and v with magnetic vector along y are in the ratio 3:1.

The (X) system is considered next. The strain is along the x direction but the tables are based on a coordinate system whose z axis is the direction of strain. A change in coordinates is made so that the chromium vacancy system is along the z' direction, the radiation is viewed along z' with magnetic vector along x'. The excited orbital is now $^4T_{2g}\xi$. Table II shows that the transitions from the upper and lower excited levels of (X) are again in the ratio 3:1.

It is not surprising that the magnetic-dipole pattern is the same from (X) and (Z) since in both cases the magnetic-dipole vector of the radiation is perpendicular to the strain.

For the (Y) system the magnetic-dipole vector is along the direction of internal strain and the pattern will be different. A change of coordinate systems is again appropriate; the direction of the strain is now z'' and the light is viewed along y'' with magnetic vector along z''. From Tables I and II the transitions from the upper and lower levels are in the ratio 0:4.

Summing over all three systems, the strengths of the magnetic-dipole transitions at 6992 Å (from the upper levels of the three representative systems) and at 7038 Å (from the lower levels) are equal.

A calculation of the relative strengths of the same electric-dipole lines can be made in a similar manner using Tables III and II.

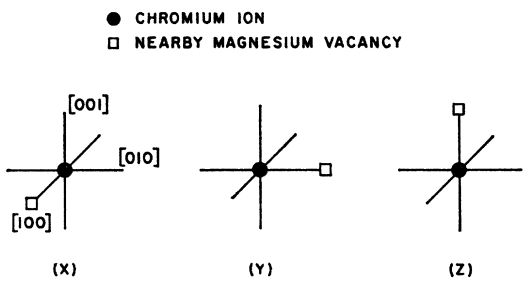

FIG. 10. The three representative chromium-vacancy systems used in the calculation of radiation patterns.

TABLE III. Dependence of excited $^4T_{2g}$ orbital on polarization of **E** for odd perturbation $T_{1u}\gamma$.

Polarization of **E**	Excited $^4T_{2g}$ orbital
x	$^4T_{2g}\eta$
y	$^4T_{2g}\xi$
z	None

Consider the electric-dipole radiation from the (Z) system emitted in the x direction with electric vector along z. The odd perturbation is along z and Table III shows that no $^4T_{2g}$ orbital is excited and hence no electric dipole radiation with z polarization is emitted by (Z).

By symmetry, the electric-dipole radiation in the x direction with z polarization emitted by (X) and by (Y) are identical. Consider the (X) system. A change to the primed coordinate system is appropriate. Polarization is now along y' and the $^4T_{2g}\xi$ orbital is excited. Table II shows that the strengths of the electric-dipole transitions from the upper and lower levels of (X) and (Y) are in the ratio 3:1. The strengths of the electric dipole 6992- and 7038-Å lines are, then, in the ratio 3:1. Since this ratio is different from that for magnetic-dipole transitions this difference can be used to determine the dipole nature of the transitions, and this is the basis for test (a).

If uniaxial pressure is applied externally along the z direction, the transitions from the upper and lower ^2E_g levels of (Z) are further separated while the corresponding transitions from the (X) and (Y) systems come closer together. This separation of the levels of

(Z) from those of (X) and (Y) is schematically shown in Figs. 11. We do not know the actual arrangement of the crystal environment so we do not know how much volume compression is introduced by the externally applied pressure. We assume that the level shift is as indicated on Fig. 11, that is, that the levels are shifted along a linear extrapolation curve. We can expect that the 7038-Å splitting will be close to that inferred from Fig. 11, but deviations may be found in the 6992-Å splitting. The theoretical splitting and intensities of the magnetic-dipole and electric-dipole transitions polarized both parallel and perpendicularly to the direction of external stress are shown in Figs. 4 and 5. The intensity units for magnetic- and electric-dipole transitions are different, but in each type of transition the same unit is employed for both the 6992- and 7038-Å lines.

Under a strong magnetic field, H_0, both lines show distinctive Zeeman patterns. The Zeeman patterns are theoretically calculated by summing over the individual patterns of the three representative systems. Tables I and III are again used but now spin-orbit matrix elements for individual $\bar{M}_s$ and M_s values must be used. The theoretical Zeeman patterns are shown in Figs. 6–9. The same intensity units as those employed in Figs. 4 and 5 are used in these theoretical Zeeman patterns. In calculating these patterns the values of g in the ^2E_g state were assumed to be sufficiently close to the ground state value so that no additional broadening or splitting due to a difference in g value need be considered. This assumption appears to be experimentally justified.

DISCUSSION OF RESULTS

Since the 6992- and 7038-Å lines do not split under pressure along [111], and since the ratio of their intensities varies as the Boltzmann factor with temperature, these lines come from the splitting of the ^2E_g level of chromium ions by a vacancy along the fourfold symmetry axis. The three experimental tests made to determine the dipole nature of the radiation are discussed below and indicate that the fluorescence is an admixture of magnetic-dipole and electric-dipole transitions.

Measurements of the intensities of the 6992- and 7038-Å lines suggest that a measurable amount of electric-dipole radiation occurs in these transitions.

The pressure induced splitting of the 6992- and 7038-Å lines would seem to indicate an admixture ratio of electric-dipole to magnetic-dipole transition of approximately $\frac{3}{2}$ if we use the intensity units employed in describing the theoretical patterns. It is interesting to note that the experimental splitting of the 6992-Å line is as inferred from the extrapolation curve of Fig. 11, but both split components are shifted to the red of the unsplit line.

When $\mathbf{H}_0\|[001]$ and $\mathbf{E}\|\mathbf{H}_0$, $\mathbf{H}\|[010]$, the theoretical

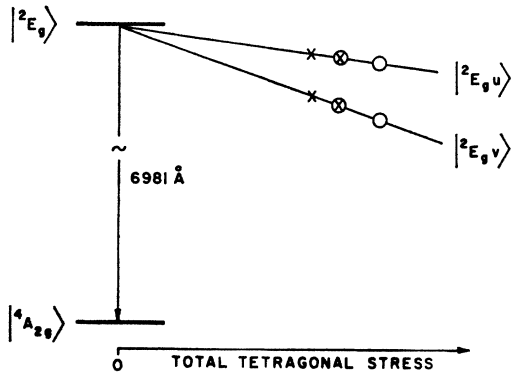

FIG. 11. Schematic representation of the splitting and shift of the ^2E_g level under tetragonal stress caused by the vacancy. The ⊗ symbols represent the positions of the levels from all three representative systems in the presence of internal stress only, and these levels give rise to the 6992- and 7038-Å lines. ○ represents the displaced position of the levels from the (Z) system under additional externally applied stress along z, and × represents the displaced position of the levels from the (X) and (Y) systems under additional externally applied stress along z. The separation of ○ and × levels give rise to the apparent splitting.

Zeeman pattern is the same for electric- and magnetic-dipole transitions, and is in excellent agreement with experiment. When $\mathbf{H}_0\|[001]$ and $\mathbf{H}\|\mathbf{H}_0$, $\mathbf{E}\|[010]$, where the theoretical Zeeman patterns are not the same, we can obtain good agreement between theory and experiment if we use the abovementioned ratio of electric-dipole to magnetic-dipole transitions. The Zeeman patterns found when $\mathbf{H}_0\|[111]$ are seen in Figs. 8 and 9. It is not necessary to specify the direction of $\mathbf{E}$ when considering electric dipole transitions with $\mathbf{E}\perp\mathbf{H}_0$, nor the direction of H when considering magnetic dipole transitions with $\mathbf{H}\perp\mathbf{H}_0$. Once again the experimental patterns are consistent with the above mentioned ratio of electric-dipole to magnetic-dipole transitions.

The pressure-induced splittings of the 6989- and 7034-Å lines are also seen in Figs. 4 and 5. Further, the 7034-Å line, and presumably also the 6989-Å line, do not split under pressure along [111]. It is clear, thus, that these lines have symmetry properties which are identical with the 6992- and 7038-Å lines, respectively. Between 20° and 90°K the ratio of the intensities of the 6989- and 7034-Å lines again are found to vary with temperature roughly as the Boltzmann factor.

These lines increase in intensity very strongly with concentration. We cannot be very quantitative about the relation between intensity and concentration, partly because we did not have analyses of all the samples. Moreover, the details of the spectrum are known to depend on the method of preparation[1] and on the presence of impurities.[3] This is not surprising, in view of the several ways in which charge compensation can occur. However, the tendency of the 6989- and 7034-Å lines to become more prominant in the darker, more concentrated, samples is quite marked. The indication is that these are lines emitted by pairs of chromium

ions, and the model adopted is that of a pair of chromium ions on either side of a magnesium vacancy, all three being disposed along a fourfold symmetry axis. It seems likely that two Cr^{3+} ions would be accompanied by a vacancy which would compensate their extra ionic charge.

Because of the exchange interaction between the ions of the pairs, the compound ground state is split into four levels of the total spin 3, 2, 1, and 0. The excited compound state can be considered to consist of a system where one ion is excited and the other is in its ground state. The exchange interaction splits the compound excited state into two spin levels with $S=1, 2$. This is in addition to the splitting of the orbital functions of the ^2E_g level of the excited ion by the vacancy. Thus, instead of two single R lines, such as are emitted by the chromium-vacancy systems, each of the two R lines of the chromium-vacancy-chromium systems should have a splitting due to the exchange interaction which may be observable.

Since the separation of the orbitals of the ^2E_g level for both systems is caused by the same type of vacancy, the separation of the R lines should be nearly the same for the chromium-vacancy system and for the chromium-vacancy-chromium system. This is confirmed experimentally; the values for the splittings are found to be within 2% of each other.

The R lines of the pair systems are seen to have structure, which may possibly be caused by the exchange interaction. Examination of the 7034-Å line at 77°K shows that it has a component at around 1.3 Å to the red of the main line which always has around 2/7 times the intensity of the main line. Further, there is an unresolved component at around 1 Å to the blue which is indicated by the arrow in Fig. 2. The 6989-Å line also has evidence of unresolved structure.

By going to very low temperatures and thereby causing a Boltzmann depopulation in the upper levels, we can decide whether the structure on the 7034-Å line belongs to the ground or the excited state of the transition. At 1.8°K, the fractional intensity of the component at 1.3 Å to the red remains the same as at 4.2°K, while the component to the blue, which is indicated by the arrow in Fig. 2, disappears. Thus, there would appear to be a 2.0 cm^{-1} splitting of the upper state and a 2.6 cm^{-1} splitting of the ground state.

The Zeeman patterns of the 7034- and 6989-Å lines seem to be very similar to the patterns of the 7038- and 6992-Å lines. Further, although the evidence is meager, the component at 1.3 Å to the red of the 7034 Å appears to split up in a manner similar to the 7034-Å line under a strong magnetic field.

It is interesting to try to calculate the splitting of the ^2E_g level for the model assumed for the chromium vacancy system, this is, Cr^{3+}-O^{2-} vacancy. The charge discrepancy caused by the vacancy can be considered to introduce an axial crystal field. The splitting was calculated very simply using a point charge model and a value of about $+200$ cm^{-1} was obtained. The plus sign means that the u component is higher in energy than the v component when the vacancy is along the z axis. In this estimate any ionic displacement due to the formation of the vacancy is not taken into account, so that the estimated value may be considered to give an upper limit. Further, the effect on the splitting of the polarization of the oxygen ions by the charge vacancy is not considered in this calculation. The actual experimental splitting is about $+94$ cm^{-1}. The sign is in agreement with the calculation, but the magnitude is much smaller than that predicted. Only qualitative agreement with the actual splitting can reasonably be expected from the above calculation.

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