

Observation of new centers in MgO:Cr³⁺

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Emission and excitation spectra for new kinds of centers in MgO:Cr have been observed. By comparing the excitation spectra and the lifetime of these centers with the corresponding—more accurate than available in the literature—measurements relative to cubic and tetragonal ones, and by investigating the symmetry of the new centers by polarization experiments, useful information on the physical nature of the centers could be gained.

When Cr³⁺ enters as a substitutional impurity in MgO, replacing an Mg²⁺ ion, its extra charge requires that a certain number of Mg vacancies are formed to keep the crystal electrically neutral; if a vacancy is placed near to a Cr³⁺ ion one has a perturbed center whose optical properties are different from those of the unperturbed centers which are at (more or less) perfectly cubic sites. So far, from optical and electron paramagnetic resonance studies at least three different kinds of perturbed centers have been identified: the tetragonal Cr-vac center, the tetragonal Cr-vac-Cr center, and the rhombic Cr-vac center where the vacancy is placed along one of the [110] axes of the cube.¹⁻⁴ The optical properties of these latter centers are rather different to those of the previous ones and of the unperturbed centers, because the rhombic component of the crystal field causes the broad ⁴T₂ level to be lower in energy than the sharp ²E level; as a result of such level rearrangement the rhombic centers, contrary to cubic and tetragonal ones, show a broad emission band and shorter lifetime (about 35 μsec instead of about 10 msec).^{5,6} This is so because while the ⁴T₂ → ⁴A₂ emission is magnetic dipole allowed, the ²E → ⁴A₂ emission, characteristic of cubic and tetragonal centers, is spin-forbidden and becomes slightly allowed by spin-orbit mixing between ²E and ⁴T₂.

A more accurate analysis of the emission spectra, however, shows that several other centers exist^{6,7}; in particular in the present paper we will present a detailed study of two sharp emission lines at 14 295 and 14 299 cm⁻¹, respectively, of their excitation spectra, lifetime τ, and symmetry. We will also discuss the origin of the centers from which they originate.

To record the emission spectra the light from a 2-mW He-Ne laser was focused onto the crystal (provided by Spicer Ltd.) which was placed in a variable-temperature (5–300-K) cryostat, and luminescence was observed at right angles through a Spex 1401 double monochromator; in the excitation measurements the He-Ne beam was replaced by the light from a tungsten lamp, dispersed by a Jobin-Yvon

HRS4 monochromator; to measure the lifetime the laser beam was focused on a mechanical chopper and then refocused on the sample; the polarization measurements were performed at 180° along the [100] direction, setting the analyzer polaroid along various crystallographic directions and rotating the entrance polaroid. In all cases the spectra were recorded by photon counting on a Laben Modular 8000 multichannel analyzer with limiting time resolution 10⁻⁵ sec/channel: this was entirely sufficient for our purposes, because τ is of the order of 10 msec. Due to the rather low emission intensity, both excitation and lifetime measurement required rather long integration times.

In Fig. 1(a) we show the emission spectrum at 8 K, in the spectral region of the ²E → ⁴A₂ emission; the nominal Cr³⁺ concentration was 1300 ppm. One can see the R line, due to cubic sites at 14 325 cm⁻¹, the tetragonal N lines (14 299 cm⁻¹: Cr-vac; 14 215 and 14 213 cm⁻¹: Cr-vac-Cr), and some weaker emissions including the A and B lines under investigation in the present paper. As T increases [Fig. 1(b)] the partners of the N states in the split ²E state become

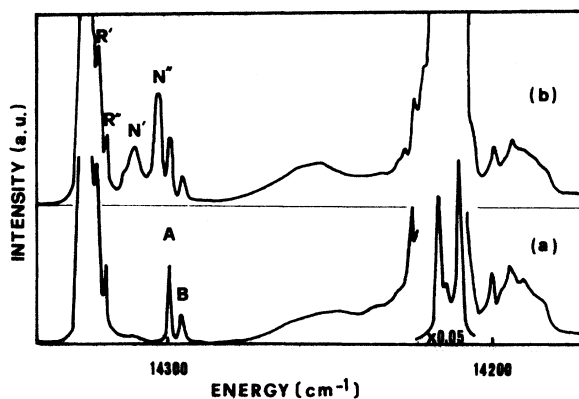


FIG. 1. Emission spectrum of MgO:Cr³⁺ at 8 (a), and 42 K (b). Energy resolution 0.3 cm⁻¹.

more and more thermally populated, and at liquid-nitrogen temperature the relative emission almost completely masks the *A* and *B* lines. We note that the relative intensity of *A* and *B* is about 4:1, and does not change appreciably with temperature: this indicates that the states from which these emissions take place are not in thermal equilibrium and must therefore belong to different centers. Such intensity ratio is in qualitative agreement with the one measured at 2 K by Larkin *et al.*⁶ Samples with different Cr concentrations (500 and 4000 ppm) gave slightly different values for this ratio: 3 and 5.5, respectively, indicating that the ratio increases with increasing the concentration.

The low-resolution (about 20-cm⁻¹) excitation spectrum at 8 K of (*A* + *B*) emissions is shown in Fig. 2(b), and for comparison the excitation spectra of the *R*- and Cr-vac-lines are shown in Figs. 2(a) and 2(c), respectively. The separate excitation spectra of *A* and *B* turned out to be very noisy, due to the high resolution required by the output monochromator, and we shall not present them. It should be noted, however, that we expect Fig. 2(b) to represent essentially the excitation spectrum of *A* (14299 cm⁻¹) which, as said, is about four times as intense as *B* (14295 cm⁻¹).

As can be seen, the excitation spectrum of (*A* + *B*) is very similar to that of the *R* line, both in regards to the position and the width of the band; in contrast the spectrum of the *N* line shows broader ⁴*T*₂ and ⁴*T*₁ bands: moreover the *N*-line spectrum shows well resolved and sharp Fano resonances⁸⁻¹⁰ on the ⁴*T*₁

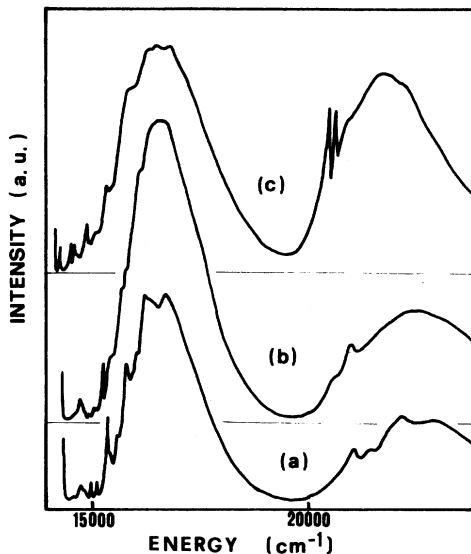


FIG. 2. Excitation spectrum of MgO:Cr³⁺ at 8 K; (a): *R* line (14325 cm⁻¹); (b): *A* line (14299 cm⁻¹); (c): Cr-vac line (14209 cm⁻¹). Energy resolution 20 cm⁻¹; the spectra are not corrected for the apparatus response.

band, which are absent in the *R* and (*A* + *B*) spectra.

If the excitation spectra are taken with higher resolution on the low-energy side of the ⁴*T*₂ band (Fig. 3) where the peaks corresponding to the sideband of the ⁴*A*₂ → ²*E* transition, the zero-phonon ⁴*A*₂ → ²*T*₁ and ⁴*A*₂ → ⁴*T*₂ transitions are observed (see Table I), the similarity between (*A* + *B*) and cubic centers is also evident, while the spectrum of Cr-vac centers is again quite different.

Now we can try to understand the physical nature of the *A* and *B* centers. From the three kinds of spectra we have presented, it is evident that the *A* and *B* emissions are due to Cr³⁺ ions which are less perturbed than the Cr-vac complex: in fact the sharp emissions (originating from the low-energy component of the split ²*E* state) are shifted only about 30 cm⁻¹ with respect to *R* line, while the corresponding *N* line is about 115 cm⁻¹ apart; the close similarity of the excitation spectra of *R* and (*A* + *B*) lines also implies little disturbance. Since the lifetime τ for a ²*E* zero-phonon state is strongly affected by the departure from inversion symmetry at the Cr³⁺ site,⁶ the fact that *A* and *B* centers are less disturbed is also confirmed by lifetime measurements at low tempera-

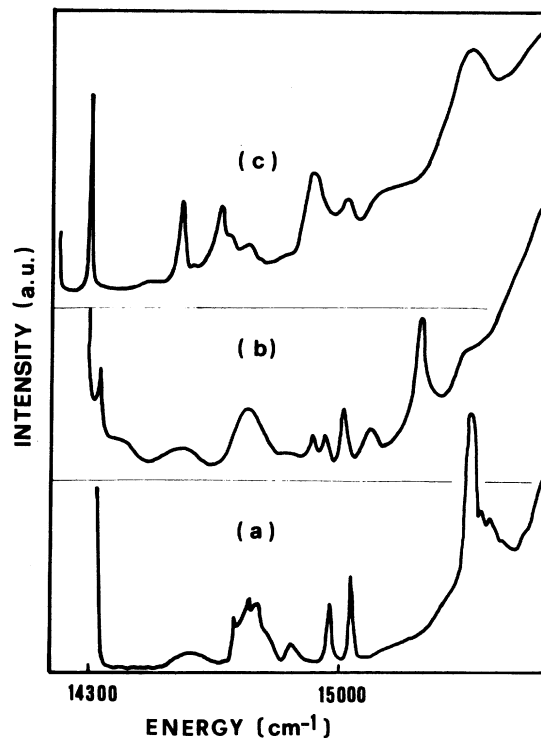


FIG. 3. Low-energy side of the excitation spectra of MgO:Cr³⁺ at 8 K. (a): *R* line, resolution 3 cm⁻¹; (b): *A* line, resolution 12 cm⁻¹; (c): Cr-vac line, resolution 5 cm⁻¹. (b) was obtained as an average of several spectra, and contrary to (a) and (c) its noise level is appreciable and is roughly equal to four times the thickness of the drawing.

TABLE I. Energies and bandwidths of the lower excited states of various centers in MgO:Cr³⁺. Units in cm⁻¹. (zpl=zero-phonon line; bm=band maximum; and bw=bandwidth.)

State	Cubic centers	Cr-vac centers	(A + B) centers
² E (zpl)	14325 ± 1	14209 ± 1 14303 ± 1	14295(B) ± 1 14299(A) ± 1 14323(A?) ± 10
² T ₁ (zpl)	14976 ± 3 15034 ± 3	14554 ± 5 14660 ± 5 15015(?) ± 10	14925 ± 15(² T ₁ ?) 14955 ± 15(² T ₁ ?) 15004 ± 15(² T ₁ ?) 15092 ± 15(² T ₁ ?)
⁴ T ₂ (zpl)	15358 ± 10	14915 ± 10	15225 ± 10
⁴ T ₂ (bm)	16650 ± 50	16800 ± 50	16720 ± 50
⁴ T ₂ (bw)	1800 ± 100	2400 ± 100	1900 ± 100

ture, whose values for *R*, *N*, *A*, and *B* lines are reported in Table II: $\tau(A)$ and $\tau(B)$ are intermediate between $\tau(R)$ and $\tau(N)$.

As for the symmetry of the *A* and *B* centers, we think that our data indicate tetragonal symmetry. In fact, as mentioned, a rhombic disturbance has drastic effects on the optical spectra: the ²E level of the rhombic Cr-vac complex is left practically at the same energy as in the cubic center, while the ⁴T₂ level is shifted towards low energy of about 1700 cm⁻¹ and is actually lower than ²E.¹¹ In the *A* and *B* centers, the zero-phonon level of the ⁴T₂ state is shifted of only about 130 cm⁻¹ and the ²E state of about 30 cm⁻¹: this seems to suggest that *A* and *B* are tetragonally distorted, by analogy to what happens in the *N* centers. In order to test more directly the symmetry of the centers, we performed polarization experiments as described above, following the method of Henry *et al.*¹¹ Their method has the advantage of being independent of the dipole nature (magnetic or electric) of the transitions and to provide simple formulas for $I(\theta)$, θ being the angle between the axis of the entrance polaroid and the [100] axis of the crystal. If the analyser's axis is in the [100] direction, we have *tetragonal centers*

$$I(\theta) = K + L \cos^2\theta; \quad K, L = \text{const} \quad (1)$$

TABLE II. Lifetime of some emissions of MgO:Cr³⁺ at 8 K. For reference see Fig. 1.

Emission	Lifetime (msec)
<i>R</i>	11.3 ± 0.1
<i>R''</i>	9.6 ± 0.4
<i>A</i>	9.8 ± 0.2
<i>B</i>	9.0 ± 0.2
<i>N</i> (Cr-vac)	8.6 ± 0.1

rhombic centers

$$I(\theta) = K' + L' \cos^2\theta; \quad L' \leq K' \quad (2)$$

If the analyzer's axis is in the [110] direction, we have *tetragonal centers*

$$I(\theta) = \text{const} \quad (3)$$

rhombic centers

$$I(\theta) = C + D \sin(2\theta); \quad C, D = \text{const.} \quad (4)$$

The data relative to the [100] analyzer setting are shown in Fig. 4, where the data relative to the Cr-vac (14303 cm⁻¹) center are included for comparison. It is evident that the *B* line is tetragonally polarized, its degree of polarization being even higher than Cr-vac's; on the other hand, even though the data rela-

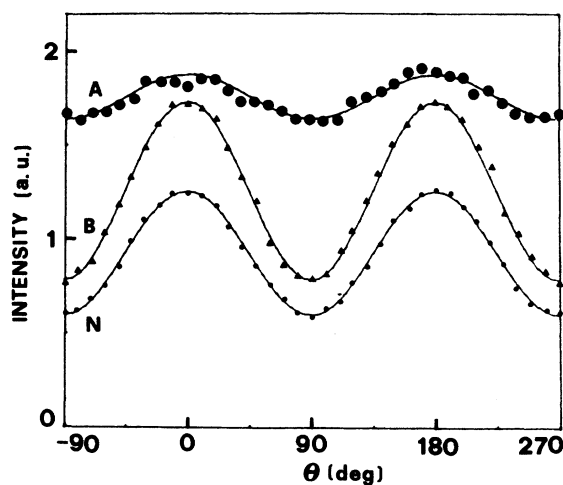


FIG. 4. Emission intensity of *A*, *B*, and *N*₂(Cr-vac) lines, (arbitrary units), as a function of the angle θ (see text) at 8 K. Full lines are the plot of Eq. (1) with the following values of the ratio K/L : for *B* line, $K/L = 0.83$; for *A* line, $K/L = 7$; for *N*₂ line, $K/L = 0.91$.

tive to A can be fit well with an expression like Eq. (1), its degree of polarization is much smaller and could even be due to residual spurious polarization of the apparatus.

As regards the spectra relative to the [110] analyzer setting, $I(\theta)$ was constant within experimental error for all emissions; this is not completely discriminatory because even the rhombic centers have small degree of polarization.¹¹

Further information on the symmetry of the various centers could, we hope, be gained by recording the electron-paramagnetic-resonance spectra of our samples, which however turned out to be highly entangled and could not be used to discern the various centers.

As to the specific nature of the centers, we note that Glass⁴ observed three sharp emission lines at 6999, 7002, and 7008 Å (14288, 14281, and 14269 cm⁻¹, respectively) after heat treatment at $T = 900^\circ\text{C}$ in air, or after doping with lithium; he attributed such lines to tetragonal centers due to hole trapped on an O⁻ ion adjacent to a cation vacancy in a Cr-vac complex. Such a center is electrically neutral and the Cr³⁺ ion is much less perturbed than in the pure Cr-vac center. We expect the Cr³⁺ ion to be even less perturbed if the vacancy is substituted by a monovalent positive ion such as Na⁺, K⁺, Li⁺: this seems to be the case for the A and B centers, whose emissions are closer to the R line than those observed by Glass. This hypothesis appears to be confirmed by an impurity analysis performed on our sample which showed it to contain traces of Na and K, in addition to negligible quantities of Rb and Cs; the measurements were not, unfortunately, reliable enough to establish a quantitative comparison between the observed A and B intensities and the measured K and Na concentrations. Moreover, even if we had measured the concentrations with precision it is not certain *a priori* that K⁺ and Na⁺ have the same affinity with the Cr³⁺ ion, thus again making problematic a quantitative comparison between concentration and intensities.

It becomes then tempting to assign the A and B emissions to Cr-Na and Cr-K centers. The presence of Na and K impurities in MgO:Cr³⁺ samples provid-

ed by Spicer had previously been detected by O'Donnell *et al.*¹² It should also be noted that the Cr- Me^+ ($Me = \text{Na, K}$) center is electrically neutral and as such its formation should be strongly favored during the crystallization process.

As regards the fact that the degree of polarization of A emission—if any—is much smaller than B 's, it is at least qualitatively consistent with the hypothesis that A and B emissions arise from Cr-Na⁺ and Cr-K⁺ centers, respectively; in fact the ionic radii of Mg²⁺, Na⁺, and K⁺ are 0.65, 0.98, and 1.33 Å, respectively: it is then to be expected that the Na⁺ ion produces a less distorted Cr- Me^+ center than K⁺ does, since the ionic radius of the latter is a factor of 2 larger than Mg²⁺'s. It would then be expected that B is much more polarized than A .

Finally, we should ask ourselves what has happened to the split partners of A and B lines (i.e., the equivalent for A and B centers of the N' and N'' lines of Fig. 1). In the excitation spectrum of Fig. 3(b) we can observe a peak at more or less the same energy as the R line, and it is reasonable to think that such a line is due to absorption of the unresolved partners. In emission such states could not be observed because they are probably masked by the extremely stronger R line. The R' and R'' lines of Fig. 1 cannot correspond to these states, because their temperature behavior indicates that they originate from centers other than A and B .

In conclusion, in the present paper we have presented evidence and detailed study of new interesting emissions in MgO:Cr³⁺. The excitation spectra indicate that the emissions originate from a perturbed Cr³⁺ ion; lifetime and polarization measurements indicate that the emissions could possibly originate from Cr-Na⁺ and Cr-K⁺ centers whose monovalent ion substitutes for Mg²⁺ ions placed at sites of tetragonal symmetry with respect to the Cr³⁺ ion.

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