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LOCALISED ELECTRONIC STATES OF DEFECT AGGREGATES IN NEUTRÔN IRRADIATED MAGNESIUM OXIDE

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Abstract. — The alkaline earth oxides have the same crystal structure as the alkali halides and consequently defects with electronic states and symmetry properties analogous with the M- and R-centers are observed after neutron irradiation. The divalent nature of the host lattice also offers additional potential for electron trapping: in this respect the R-like centres have been especially interesting. The application of uniaxial stress techniques has confirmed that optical zero-phonon lines at 5 248 Å, 6 419 Å and 6 490 Å are associated with such centres. The line at 5 248 Å is strongly dichroic under stress at 4 °K and the results are indicative of E → A transitions. The lack of such dichroic behaviour in the 6 419 Å and 6 490 Å lines confirm that these lines are associated with A → E transitions. Calculation of the electronic states of these trigonal defects suggest that the 5 248 Å, 6 419 Å and 6 490 Å lines are due to clusters of three anion vacancies lying in a (111) plane and containing 5, 6 and 7 electrons respectively.

I. Introduction. — The alkaline earth oxides have the simple rock-salt crystal structure. Consequently intrinsic lattice defects produced by irradiation are expected to be analogous with those observed in the alkali halides. However, the poor quality of commercially available single crystals of these oxides, together...
with the ineffectiveness of polarized bleaching techniques and the resistance of the oxides to damage by ionizing radiation have considerably hindered the progress towards understanding the electronic states of the intrinsic lattice defects. Detectable concentration of intrinsic lattice defects are in fact observed only in crystals exposed to fast neutron irradiation. Under such conditions almost equal numbers of anions and cations are displaced in magnesium oxide. Consequently, numerous complex defects are readily identified by their electron spin resonance spectrum in addition to the copious numbers of F-centres [1, 2].

The optical absorption spectrum of neutron irradiated magnesium oxide is not yet completely understood. The F-band is known to be centred at 2.500 Å [3, 4, 5]; however, a peak observed at 5.740 Å has not yet been assigned to any particular defect species. Bands at 9.500 Å and 3.500 Å show well resolved zero-phonon lines and phonon-assisted structure at temperatures below 77 °K. Ludlow [6] has suggested that these bands are due to transitions within the same centre: the centre has orthorhombic symmetry and [110] orientation with linear electric dipole oscillators parallel to the [110] direction. If magnesium oxide is irradiated at elevated temperatures (600 °C) or annealed at temperatures >300 °C after irradiation, then the optical absorption spectrum is much more complex consisting of many overlapping bands [2, 4, 7]. Uniaxial stress measurements on the zero-phonon lines observed at low temperatures to be associated with these bands, have indicated that defects are present in the crystals which may be analogous with the M, R and N-centres observed in the alkali halides. Some of the properties of the M and R-like centres are discussed in this paper.

In addition to the defects which have optical properties analogous with the F-aggregate defects in the alkali halides, a number of centres may be produced for which no such analogy exists. Evidence supporting the models proposed for these defects is discussed briefly.

II. Experimental procedure. — Magnesium oxide single crystals were obtained from the Norton Company, Worcester, Massachussetts, U. S. A. Specimens cleaved from large single crystal blocks were irradiated at temperatures in the range 150-600 °C in the Harwell DIDO reactor. Optical absorption measurements were made using either a Cary 14 recording spectrophotometer or a Hilger Universal 3 metre spectrograph. The uniaxial stress apparatus used at 4 °K with both the spectrometer and spectrograph have been described in the literature [7, 8]:

Electron spin resonance measurements were made at temperatures between 40-293 °K using a Varian superheterodyne spectrometer; 100 kc/s field modulation and a Fieldial regulated 9° rotatable magnet were used. Where necessary, illumination of the sample with visible or ultra-violet light was carried out in situ in the TE 102 microwave cavity via precisely machined radiation slots in the end wall of the cavity. An Osram 250 W high pressure mercury lamp was used together with a Hilger and Watts grating monochromater to select particular bleaching wavelengths.

III. Results and discussion.

(i) Studies of optical zero-phonon lines. — The general features of the optical absorption spectrum of magnesium oxide after neutron irradiation at 600 °C are shown in figure 1. The spectrum was recorded at 77 °K and the presence of many zero-phonon lines in the range 5000-7000 Å indicates that the very strong absorption in this range is due to the presence of numerous overlapping broad bands. Observation of the zero-phonon lines shown in figure 1 was first reported by Wertz et al. [2]. The half-widths of these lines are strongly sensitive to radiation dose and to thermal treatment [7]. Such variations in the half-widths are apparently associated with changes in the magnitude of microscopic strains due to the presence of dislocations and point defect in the irradiated crystals. Under conditions of high resolution phonon-assisted transitions can be seen on the high energy side of the zero-phonon line. Detailed comparisons of the phonon-assisted structure with the phonon dispersion curves obtained from slow neutron scattering measurements have been made by numerous authors [6, 7, 8].

![Graph of Optical Absorption Spectrum of Magnesium Oxide](image-url)
(ii) **Uniaxial Stress Measurements.** — The zero-phonon lines at 4684 Å and 4700 Å behave similarly under an applied uniaxial stress (Fig. 2). Analysis of the stress splitting patterns confirms that these lines are associated with defects having [110] orientations and orthorhombic symmetry with linear electric dipole oscillators along a [110] direction. Such symmetry properties are identical with those expected for M-centres; recent evidence however, suggests that the production of these defects is impurity controlled [9].

![Stress-induced splittings of the 4684 Å and 4700 Å lines at 77 °K in neutron irradiated MgO.](image)

*Fig. 2.* — Stress-induced splittings of the 4684 Å and 4700 Å lines at 77 °K in neutron irradiated MgO.

a) [100] stress of 46 kg. mm⁻²,

b) [110] stress of 41.5 kg. mm⁻² with light along [110] (σ-refers to E parallel to stress and ε refers to E-perpendicular to stress).

Similar analysis of the stress splitting patterns of the lines at 5248 Å, 6419 Å and 6490 Å show that the lines are due to A ↔ E transitions within defects having trigonal symmetries and [111] symmetry axes [7, 10]. At 4 °K the 5248 Å line is strongly dichroic under uniaxial stress (Fig. 3). Such behaviour is expected only if the E-state is the ground state since the applied stress removes the orbital degeneracy of the E-ground state and the intensity ratio between the two optical transitions will be proportional to \( \exp(-\Delta E/kT) \), \( \Delta E \) being the stress induced ground state splitting. The compared intensities under stress at 77 °K and 4 °K shown in figure 3 are consistent with those expected for a trigonal defect with optical dipole moments along the [110] and [112] directions in the plane perpendicular to the trigonal axis. Ground state splittings of 15 cm⁻¹ have been achieved under stress and for this splitting a population ratio between the two levels will be of order 1/300 at 4 °K. The absence of one component at 4 °K is in accord with these ideas and hence it is concluded that the defect associated with the 5248 Å line has trigonal symmetry and the transition is from an E-ground state to an A-excited state. No such dichroism is observed for the 6419 Å and 6490 Å lines and the defects associated with these lines presumably have A-ground states.

![Theoretical and Experimental Dichroism](image)

*Fig. 3.* — a) Dichroism expected for an \( E \rightarrow A \) transition of a trigonal centre with [110] and [112] dipoles and stress along [100].

b) Experimentally observed behaviour of 5248 Å zero-phonon line under [100] stress at 50 kg. mm⁻².

Models for the centres associated with these three zero-phonon lines consist of three anion vacancies forming an equilateral triangle on the (111) plane and containing different numbers of trapped electrons: six are required for electrostatic neutrality. It is now instructive to use a molecular orbital approach to construct the most likely set of one electron levels for defects with appropriate symmetry containing five, six or seven electrons. The author has shown that for a five electron centre the ground level is

\[
2E[(1 a_1)^3 (1 e)^2]
\]

transitions appropriate to the 5248 Å line may then
occurs to a $2A_1[(1a_1)(1e)^4]$ excited state. On the basis of similar molecular orbital calculations, the ground states of defects containing six and seven electrons may be shown to be $^1A_1$ and $^2A_1$, respectively: the expected excited states are then $^1E$ and $^2E$. The optical zero-phonon lines at 6 419 Å and 6 490 Å have been assigned to $R$-like centres containing six and seven electrons respectively [11].

The discussion given above suggests that the defect responsible for the zero-phonon line at 5 248 Å should be paramagnetic. Since $S = \frac{1}{2}$ for this five electron defect, the electron spin resonance spectrum for such a defect is expected to overlap the $F$-centre spectrum. As a result, and since the $F$-centre concentration is normally much larger than that of other defects, this spectrum has not previously been reported. However, in crystals irradiated at 600 °C the concentration of aggregate centres is approximately equal to the $F$-centre concentration. Recent measurement at $X$-band have shown that in such crystals, defects are present which have anisotropic $g$-tensors and which might be associated with the defect in question. The lines occur at higher $g$-values than the $F$-centre, but at $X$-band the separation is such that the detailed $g$-tensor anisotropy cannot be fully investigated. At $G$-band our investigations are not complete, since the orientation dependence along the $[100]$ axis is shown in figure 4; the results are in accord with centres with trigonal symmetry. Preliminary $g$-values for this defect are $g_{11} = 2.000$ and $g_1 = 2.018$; further examination of this spectrum are currently in progress. An enormous paramagnetic Faraday rotation pattern has also been associated with the 5 248 Å zero-phonon line. Although much remains to be done both theoretically and experimentally, the accumulated evidence for the proposed model of this defect is quite compelling.

(iii) ELECTRON SPIN RESONANCE STUDIES. — After long periods of irradiation numerous trapped hole centres may be recognized by their paramagnetic resonance spectrum [1]. In addition, the authors have recently shown that paramagnetic trapped electron centres may also be present. One such centre [13], $F_T$-centre (*), is believed to consist of two next nearest neighbour $F$-centres separated by a $Mg^{2+}$ vacancy: the defect therefore has a tetragonal axis along [100]. The $F$-centres are coupled by an isotropic exchange interaction of the form:

$$JS_i S_j = \frac{1}{2}(JS(S+1) - S_i(S_i+1) - S_j(S_j+1))$$

where $S$ is the total spin and can take values $S = 0$ or $S = 1$. The triplet state is empty at 4 °K but almost fully occupied at 300 °K and comparison of the experimental signal intensities give a value for $J/K = 80 \pm 10$°K. The paramagnetic resonance spectrum, shown in figure 5, may be described by a spin-Hamiltonian of the form

$$\mathcal{H} = g\beta H.S + D(S^2 - 1/3 S(S+1))$$

where $S$ is the measured parameters are $g = 2.0030 \pm .0005$ and $D = 307 \pm 3$ Gs.

Assuming that the anisotropic interaction parameter $D$ is accounted for entirely by dipole-dipole coupling the estimated separation between the $F$-centers is 4.07 Å since $D = 111 g^2 \beta^2/(10 r_i^3)$. This value is consistent with the oxygen-oxygen separation along [100] of 4.2 Å in magnesium oxide.

A second triplet state resonance has been observed for a defect with orthorhombic symmetry and [110] axes of symmetry. The exchange interaction is smaller than that of the $F_T$-centre. Due to overlap with other lines, it has not been possible to measure accurately the values of the Hamiltonian parameters. Approximate values available at present are $g = 2$, $D = 140$ Gs and $E = -30$ Gs. Assuming weak dipole-dipole coupling we find $r_{ij} = 6.7$ Å which suggests that the defect consists of two exchange coupled $F$-centres in next-nearest neighbour association along the [110] direction. For purposes of identification we designated this centre the $F_R$ centre where the subscript $R$ is intended to refer to the rhombic symmetry of the defect.

The two defects referred to above are extremely unstable to annealing treatment: a few minutes at

(*) This nomenclature is that used by Tanimoto et al. [13] to describe an identically similar defect in calcium oxide.
temperatures of 400 °C is sufficient to reduce the electron spin resonance signal intensities to undetectably low levels. In addition, such treatment results in the formation of \( F_2 \)-centres at the expense of \( F \)-centres. The model proposed by Wertz et al. [12] for this defect was an electron trapped at a cation-anion vacancy pair. The only evidence for this was the \( g \)-value of the \( F_2 \)-centre and the line shape of the e. s. r. line in powders. Recent measurements by the author at Q-band confirm that the centre has an axially symmetric \( g \)-tensor: the appropriate values are \( g_\perp = 2.0004 \) and \( g_\parallel = 2.0017 \). It is to be noted that \( Ag_\parallel = +0.0017 \) indicating that the spin orbit coupling constant is negative. This is similar to the situation in the magnesium oxide \( F \)-centre [5, 14]. A complete analysis of the hyperfine structure of this centre has not yet been possible although there is reason to believe that the magnitude of the isotropic component of the hyperfine interaction is larger than in the \( F \)-centre. This evidence strongly supports the original model proposed by Wertz for this defect.

Recent observations by King and Henderson [10] that the \( F_2 \)-centre may be optically bleached has clarified the controversial ideas related to the position of the \( F_2 \)-band [2, 4]. The efficiency of bleaching of the \( F_2 \)-centre as a function of photon wavelength is shown in figure 6. This curve was obtained by monitoring the decay of the \( F_2 \)-centre concentration as a function of the bleaching time with monochromatic radiation of wavelengths in the range 2 500 Å - 6 500 Å. For this purpose the amplitude of the \( F_2 \)-centre resonance line was compared with that of the Mn\(^{2+} \) lines since the latter do not change during the « in situ » experiments. The curve shows that a peak bleaching efficiency is obtained at 3.7 eV. As discussed by King and Henderson [10] this behaviour is consistent with the removal of the \( F_2 \)-centre electron from the ground state into the conduction band. Such behaviour is predicted by simple calculations of the energy levels of the \( F_2 \)-centre electron which show that only one bound state exists below the top of the conduction [15].

IV. Conclusions. — The defect structures discussed in this paper are summarized in figure 7. The
uniaxial stress measurements convincingly demonstrate that centres analogous with the \( M \), \( R \) and \( N \) centres in the alkali halides may exist in the alkaline earth oxides. The lines at 4 684 Å and 4 700 Å have extremely similar properties and the most reasonable models for these two defects are shown in figures 7a and 7b. The results suggest that one \( R \)-like centre containing 5 trapped electrons should be paramagnetic: preliminary experimental evidence confirms this suggestion.

In addition, centres exist for which no analogue exists in the alkali halides. Three of these centres, the \( F_0 \), \( F_R \) and \( F_2 \)-centres have simple symmetry properties that are readily adduced from the paramagnetic resonance spectra. The optical absorption in the \( F_2 \)-centre occurs with maximum efficiency at 3.7 eV: the transition apparently occurs between a 1 S-Like ground state and the conduction band.

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