PARAMAGNETIC RESONANCE OF OXYGEN IN ALKALI HALIDES

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Alkali halide crystals grown from the melt exhibit a paramagnetic resonance spectrum at low temperatures which we have attributed to oxygen and have investigated in detail in the chlorides, bromides, and iodides of sodium, potassium, and rubidium. The concentration of these paramagnetic centers can be greatly enhanced by heating the crystals in an oxygen atmosphere, and it can be reduced to undetectable amounts by heating the crystals in other gases, such as hydrogen, halogen, water vapor, or in vacuum.

The paramagnetic resonance spectra indicate that the nuclei to which the resonant electron is bound do not give rise to hyperfine splitting and consequently must have spin 0, as does O^{16}. However, a weak hyperfine interaction with four equivalent alkali nuclei can be partially resolved under favorable circumstances in potassium and rubidium halides. The g tensor has orthorhombic symmetry with the axes parallel to [110], [1$\bar{1}$0], and [001]. These facts together rule out a monatomic center. The diatomic molecule ion O_2^- is the most probable model. It substitutes for a halide ion as shown in Fig. 1.

The ground state of O_2^- is a $^2\pi$ state according to the occupation of the levels given in Fig. 2.

The hyperfine interaction with four equivalent alkali nuclei indicates that in the potassium and rubidium halides the $p\pi$ orbital is oriented as shown in Fig. 1. This fact is substantiated by the analysis of the g tensor.

Explicit formulas for the g factors have been derived on the basis of the level scheme shown in Fig. 2. No assumption was made about the relative order of the spin-orbit splitting and the crystal field splitting. Mixing between the π_g levels and all others was included only in second order. Simplified versions of the formulas so obtained are

$$g_\zeta = g_e + 2\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} l, \tag{1}$$

$$g_\xi = g_e\left(\frac{\Delta^2}{\lambda^2 + \Delta^2}\right)^{1/2} - \frac{\lambda}{E}\left[-\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2}\right.$$
$$\left. - \frac{\Delta}{(\lambda^2 + \Delta^2)^{1/2}} + 1\right], \tag{2}$$

$$g_\eta = g_e\left(\frac{\Delta^2}{\lambda^2 + \Delta^2}\right)^{1/2} - \frac{\lambda}{E}\left[\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2}\right.$$
$$\left. - \frac{\Delta}{(\lambda^2 + \Delta^2)^{1/2}} - 1\right], \tag{3}$$

where ξ is chosen along the $p\pi$ function, and ζ is the internuclear axis. Here λ is an effective spin-orbit splitting of the molecule ion in the
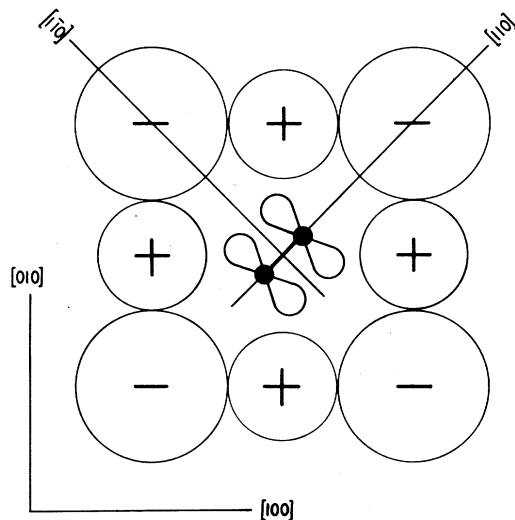

FIG. 1. An O_2^- molecule ion substituted for a halide ion in an alkali halide crystal. The orientation of the p function of the unpaired electron corresponds to the case of the potassium and rubidium halides.
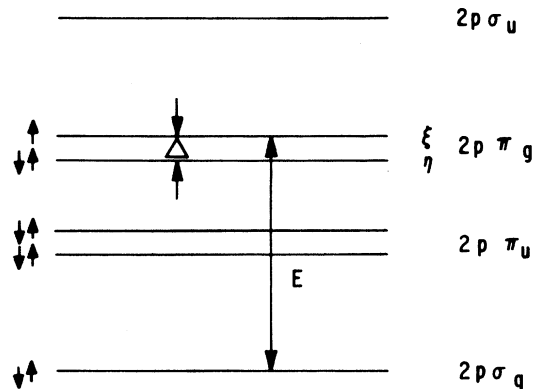

FIG. 2. Occupation of the electronic levels of O_2^- in the ground state.

crystal, Δ is the $2p\pi_{g\xi}$-$2p\pi_{g\eta}$ separation and E is the $2p\pi_g$-$2p\sigma_g$ separation. Further, l represents a correction to the angular momentum about ζ caused by the crystal field; l is unity for the free molecule ion. The first two terms in (1) and the first term in (2) and (3) are exact. All second-order terms except those from the $2p\sigma_g$ level have been omitted. The matrix elements in the second-order terms kept have been replaced by those appropriate to the isolated molecule ion.

The calculation shows that g_η exceeds g_ξ. From the experimental g tensors we can thus infer that the $p\pi$ functions point along $[1\bar{1}0]$ in the potassium and rubidium halides (as depicted in Fig. 1), but along $[001]$ in the sodium salts. These assignments are consistent with the hyperfine data.

A typical example is furnished by KCl with $g_\zeta = 2.4359$, $g_\xi = 1.9512$, and $g_\eta = 1.9551$. The corresponding values of λ/Δ and λ/E are 0.23 and 0.0025 and l is 1.04. A value of λ taken from atomic oxygen, 226 cm^{-1}, when combined with these values for λ/Δ and λ/E, leads to separations Δ and E about four times larger than might be expected in comparison with the well-investigated (halogen)$_2^-$ molecule ions.[1,2] However, in O_2^- the predominant contribution to λ arises probably from an O^- configuration which would result in a λ several times smaller than for atomic oxygen. This would lead to quite reasonable values of Δ and E.

The optical absorption near 4.9 ev observed in similarly treated crystals by Rolfe,[3] and the associated fluorescence emitted between 1.8 ev and 2.8 ev studied by Honrath[4] and Ewles and Barmby[5] may well be due to this O_2^- center. However, confirmation of this proposal would require simultaneous study of optical absorption and paramagnetic resonance.

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A full account of the present work will be published in a forthcoming paper.

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DEPENDENCE OF SECONDARY ELECTRON EMISSION ON CRYSTAL ORIENTATION

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The dependence of secondary electron emission on the angle of incidence of primary electrons has been examined using single crystals of MgO and LiF. An unexpected dependence on crystal orientation has been observed. A series of maxima and minima occurs superposed on the previously reported[1] increase in secondary emission with increasing angle of incidence. The maxima have been found to represent as much as 20% of the total secondary emission yield under some conditions and therefore contribute substantially to the total number of secondary electrons. The origin of the maxima and minima is not well understood. However, they do not appear to result from a diffraction effect since the angular positions of the maxima are not dependent on the energy of the primary electrons.

The secondary emission measurements were made using sealed-off tubes under clean high-vacuum conditions with pressures of 10^{-9} mm Hg or less. The tubes included an electron gun producing a collimated electron beam of 3° divergence, a graphite-coated secondary electron collector, and a stabilizing filament for flooding the crystals with low-energy electrons. A target holder was suspended from two rods through the side of the tube so that by rotating the tube about the axis of the rods the angle of incidence could be varied. The crystal and target holder remained fixed in position under the influence of gravity.

The MgO and LiF single crystals were cleaved