imation and without the large numbers of adjustable parameters, may furnish a more satisfactory (and satisfying) approach.

Since this method allows for inclusion of specific interactions then data analysis using the technique might furnish a better understanding of the basic physical mechanisms operating in a metal. Attempts in this direction have recently been made for zinc[10] and beryllium,[10, 11] with promising results.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 4 15 AUGUST 1971

Theory of Axially Symmetric O^- Defect Centers in Alkali Halides

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An analysis is presented that permits a direct determination from electron-spin resonance (ESR) data of crystal-field splitting energies and also identifies which Kramers's doublet lies lowest for axially symmetric O^- defect centers. The analysis is such as to make it unnecessary to solve the secular equation for both the crystal-field and spin-orbit interaction.

Electron-spin-resonance (ESR) absorption measurements made at 4.2 °K on alkali halide crystals subjected to electrolytic coloration followed by uv photolysis have demonstrated the existence of new paramagnetic centers. These centers have axial symmetry and are believed to be O^- ions that substitute for halide ions.[1,2] The first theoretical analysis undertaken on the spectral parameters of this system is that due to Vannotti *et al.*[2,3] We would like to draw attention to two aspects of their analysis: (i) The energy of the $| P_z \rangle$ level given in Ref. 3 for the case of an orthorhombic crystal field [Eq. (5)] is not an exact root of the corresponding secular equation, a point which we shall discuss; (ii) it is difficult to establish the $| P \rangle$ energy-level sequence. In order to obtain this sequence, results due to Schoemaker and Boesman[4] were used.

In this paper, a mathematical procedure is developed which provides for exact solution to the crystal-field splitting energies of the aforementioned problem for ESR data, without any *a priori* assumption in regard to which Kramers's doublet lies lowest.

Under the combined action of an orthorhombic crystal field

$$\hat{\mathcal{H}}_{cf} = E[L_z^2 - \tfrac{1}{3} L(L+1)] + (\Delta/2)(L_x^2 - L_y^2) \qquad (1)$$

and the spin-orbit interaction

$$\hat{\mathcal{H}}_{LS} = \lambda \vec{L}\vec{S} \,. \qquad (2)$$

The energies of the three Kramers's doublets resulting from the $2p^5$-^2P term of the free O^- ion are given by

$$W^3 - (\tfrac{1}{3} E^2 + \tfrac{1}{4}\Delta^2 + \tfrac{3}{4}\lambda^2) W + \tfrac{2}{27} E^3 - \tfrac{1}{6} E\Delta^2 + \tfrac{1}{4}\lambda^3 = 0, \qquad (3)$$

and the corresponding eigenvectors take the form[5]

TABLE I. Spin-Hamiltonian parameters and crystal-field splittings of O^- centers in some alkali halides.

Crystal	$g_{\parallel}$	$g_{\perp}$	C_1	C_2	λ/E	λ/W	l
NaI	1.9769	2.2931	±0.9936	±0.07950	−0.176	+0.259	1.002
KCl	1.981	2.258	±0.9947	±0.07237	−0.160	+0.236	0.955
KBr	1.987	2.226	±0.9962	±0.06182	−0.133	+0.198	0.970
KI	1.9733	2.3023	±0.9927	±0.08503	−0.191	+0.278	0.974
RbI	1.9733	2.2888	±0.9927	±0.08503	−0.191	+0.278	0.933

$$|P^{\alpha}\rangle' = C_1 |P_z^{\alpha}\rangle + C_2 |P_x^{\beta}\rangle + C_3 |P_y^{\beta}\rangle ,$$
$$|P^{\beta}\rangle' = C_1 |P_z^{\beta}\rangle - C_2 |P_x^{\alpha}\rangle + C_3 |P_y^{\alpha}\rangle . \tag{4}$$

{In regards to the results of Ref. 3, one can check that the value $W = E[1 - (\Delta^2/2E^2)]$ is not a root of Eq. (3). }

In the case of an axially symmetric crystal field, $\Delta = 0$ and $C_2 = C_3$. Using the eigenvectors given in Eq. (4), the following expressions may be obtained for the g-tensor components by applying the Zeeman operator $\mathcal{H}_z = \mu_B \vec{H}(\vec{L} + g_e \vec{S})$:

$$g_{\parallel} = |g_e C_1^2 - 2C_2^2(g_e - 2)| ,$$
$$g_{\perp} = |g_e C_1^2 + 4lC_1C_2| , \tag{5}$$

where $C_1^2 + 2C_2^2 = 1$, and

$$\langle P_z | L_{\pm} | P_y \rangle = \mp \langle P_z | L_{\pm} | P_x \rangle = l . \tag{6}$$

The parameter l gives the matrix elements of the $L_{\pm}$ operator whose deviation from unity is to be associated with fact that the corresponding one-electron wave functions are not pure p orbitals. To avoid needless complications, we have considered λ and l to be isotropic.

In the case of an axially symmetric crystalline field, the following useful relations may be obtained from the relations between the parameters C_i without actually solving the secular equation:

$$\frac{W}{\lambda} = \frac{F^3 - 1}{3(F^2 - 1)} , \quad -\frac{2E}{3\lambda} = F - \frac{2W}{\lambda} , \quad F = \frac{C_1}{C_2} - 1 . \tag{7}$$

These relations permit a ready determination of the ratios λ/E and λ/W from ESR data (see Table I). Furthermore, with these ratios, as well as with the assumption that the sign of λ is negative,[6-8] it becomes possible to determine which of the three Kramers's doublets lies lowest. The experimental data suggest that the $|P_z\rangle$ doublet is the lowest-lying level for all of the hosts given in Table I, while the small difference between our values of λ/E and those given in Ref. 2 can be interpreted as being due to the influence of spin-orbit interaction on the $|P_z\rangle$ level. (The formula $W_z = E$ used in Ref. 2 did not take into consideration this influence.)

It should also be mentioned that for $l \neq 1$ the aforementioned theory must be considered as a less than desirable approximation. In such a case, a more appropriate approximation would consist of the use of wave functions that are eigenvectors of $\mathcal{H}_{\text{atom}} + \mathcal{H}_{\text{cf}}$ of the central atom and ligands, both modified by an unisotropic spin-orbit interaction. Even in this case, the over-all form of g-factor formula (5) would remain the same, with λ and E being considered as effective parameters in a manner similar to that done by Zeller and Känzig[9] for O_2^- centers.

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$$|P_z^{\alpha,\beta}\rangle = |L_z = 0, S_z = \pm\tfrac{1}{2}\rangle ,$$
$$|P_x^{\alpha,\beta}\rangle = (1/\sqrt{2})[\,|+1, \pm\tfrac{1}{2}\rangle - |-1, \pm\tfrac{1}{2}\rangle\,],$$
$$|P_y^{\alpha,\beta}\rangle = (1/\sqrt{2})[\,|+1, \pm\tfrac{1}{2}\rangle + |-1, \pm\tfrac{1}{2}\rangle\,].$$

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