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Magnetic Resonance Studies of F and M Centers

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Magnetic resonance studies of F centers by Holton and Blum are reported for a number of alkali halides. By means of the electron-nuclear double resonance technique (ENDOR), the wave function density $|\Phi(\vec{R}_n)|^2$ at the nuclear positions $\vec{R}_n$ are determined, in some cases through 7 shells of atoms from the vacancy. The results are compared with the calculations of Gourary and Adrian, and of Kojima which were made using the point-ion approximation. According to G and A, the wave function $\Psi_F(\vec{r})$ which is the solution of the point-ion approximation is related to the actual wave function $\Phi(\vec{r})$ at each of the nuclear sites through the equation $|\Phi(\vec{R}_n)|^2=A_n|\Psi_F(\vec{R}_n)|^2$ where A_n, the amplification factor, is characteristic of the atom in question, independent of the crystal in which the atom is found (*i.e.*, A_{Li} is the same for Li in LiF and LiCl). This hypothesis is shown to be well satisfied by using experimental values of $|\Phi(\vec{R}_n)|^2$ and theoretical $|\Psi_F(\vec{R}_n)|^2$ to deduce the amplification factors of a given nucleus in different alkali halides. This procedure indirectly tests the consistency of the $|\Psi_F(\vec{R}_n)|^2$'s.

The particular case of LiF, which has been the subject of controversy, is now well understood. The F centers in the fluorides appear to be quite like those in other alkali halides.

The experimentally observed ENDOR spectrum consists of many more lines than are predicted by simple first order perturbation theory. These may be explained by use of second order theory. Feuchtwang has shown that in the process the sign of the electric field gradient experienced by the nuclei can be obtained. The field gradients arise from four sources: (i) the missing halogen atom, (ii) the F electron, (iii) polarization of the electron clouds of the ions, and (iv) displacement of ions from their equilibrium positions. Feuchtwang shows that (iii) may be neglected compared to (iv). Evaluation of (iii) involves the integral

$$\int|\Phi|^2\frac{(3\cos^2\theta_\alpha-1)}{r_\alpha{}^3}[1-\gamma_\alpha(r)]d\tau \qquad (1)$$

where r_α and θ_α are coordinates of the electron measured from the α^{th} nucleus, and $\gamma_\alpha(r)$ is the Sternheimer antishielding factor. A similar integral without the factor $[(1-\gamma_\alpha(r)]$ is involved in calculating the so-called $b_{O\alpha}$ coefficient arising from the dipole-dipole coupling between electron spin and nuclear spin.

Feuchtwang evaluated the integral (1) by a combination of theoretical calculations for the volume outside the α^{th} ion, and the experimentally determined $b_{O\alpha}$. In this manner he can safely use an approximate wave function for Φ in the calculation since the contribution for small r_α is obtained by experiment.

Studies of M center are complicated by the presence of F and other centers. In NaF, however, Blum has found that a particularly strong M band can be made. The intensity of the electron resonance is studied during coloring by X-rays, at which time both an F and an M band are formed, and during subsequent bleaching by light in the F band, during which the F band can be bleached almost entirely, leaving only an M band. Blum concludes that no resonance is associated with the M band, a result consistent with the Van Doorn model of the M center as a pair of F centers.

DISCUSSION

Pick, H.: The reason for the change of the ESR signal when M-centers are formed is due to the exchange narrowing effect which occurs, if F-centers move together to a distance of about 4 lattice parameters. (Work of Schwoerer at Stuttgart).

Slichter, C. P.: A similar result appears to hold for LiF, for which Bray has observed

the formation of a fairly broad, Lorentzian line for heavily damaged crystals.

If *F*-centers come together in pairs, and if their electron spins form a triplet state, the resonance line will remain Gaussian, but the second moment will be smaller by a factor of 2. For progressively larger groupings, the line shape should gradually change to a Lorentzian.

Lazarus, D.: I wonder if you have any values for the lattice contraction about the *F*-center, or justification for this? From high-pressure studies of diffusion and ionic conductivity, it can be concluded that the volume of neutral vacancies is somewhat larger than the ionic volume, for both positive and negative ion vacancies.

Slichter, C. P.: One must distinguish between *F*-centers and neutral vacancies. The latter expand since the missing charge helped to hold the lattice together. With an *F*-center, two competing effects arise. The electron tries to pull the lattice in, but since it is somewhat more diffuse than the ion it replaces, it is not as effective for the close atoms. On the other hand, the missing ion possessed inner shell electrons which help to prevent a lattice contraction. The absence of these repulsive forces favors an inward collapse.

Detailed calculations have been made for the *F*-center in LiF, but different theorists have come to opposite conclusions as to which effect prevails.

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Electron Spin Resonance of Electron-Excess Color Centers in KCl Crystals

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Electron spin resonances for various kinds of electron-excess color centers have been carried out. Non-magnetism of the F' and M center is confirmed. The study of sodium-A centers verifies the model proposed by Nishimaki, Kojima and Lüty. The result on the B center shows the consistency with Mieher's *ENDOR* result.

The paramagnetism associated with the Z_3 center was found, but that of the Z_2 center could not be detected. These results are inconsistent with the proposed models by Pick and Seitz. To explain our results, two alternative models are proposed for the Z_2 center, *i.e.* a pair of divalent ions trapping two electrons, or the association of an F center and a divalent ion that has trapped an electron. The Z_3 center is proposed to be an ionized Z_2 center.

1. Introduction

The electron spin resonance study of the color centers in alkali halide crystals is very important not only for the verification of their proposed models, but also for the determination of their electronic structures. A few studies have been carried out for the electron-excess color centers other than the F center.[1)]

When the colored *KCl* crystals doped with *NaCl* are irradiated with the F light at $-30°C$, two absorption bands appear at the expense of the F band. These have been named A_1 and A_2 band, and found to arise from a common species of centers called A centers by Nishimaki, K. Kojima and T. Kojima,[2)] and Lüty,[3)] independently. They proposed a model (NKL's model) for the A center as an F center in which one of the six nearest neighboring potassium ions has been substituted by a sodium ion. Similar results are obtained for *Li*-doped *KCl* crystals.

Two absorption bands are also obtained by