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Electron Spin Resonance Studies of Donors and Acceptors in ZnO

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Electron spin resonance of acceptors due to substitutional Li, and the resonance of certain donors previously reported at $g\cong1.96$ were examined using polycrystalline samples of ZnO. It was found that the latter signal could actually be a superposition of two independent signals, one arising from the oxygen vacancy and the other from the substitutional halogen. The analysis of the resonance spectra gave for the Li acceptor $g_{\parallel}=2.0026\pm0.0005$, $g_{\perp}=2.0254\pm0.0005$, $A_{\parallel}$ (with Li^7 nucleus) $\leqq0.1\times10^{-4}$ cm^{-1} and $A_{\perp}$ (with Li^7 nucleus) $=(1.73\pm0.02)\times10^{-4}$ cm^{-1}; for the donor due to oxygen vacancy $g_{\parallel}=1.957\pm0.001$, and $g_{\perp}=1.956\pm0.001$; and for the halogen donor $g=1.960\pm0.001$. These g values are interpreted in terms of a picture in which a hole associated with the Li acceptor is localized in the valence orbital of one of the four adjacent oxygen, while the electrons trapped by the donor levels due to oxygen vacancies or substitutional halogen are shared more or less equally among the valence orbitals of the surrounding zinc ions.

I. INTRODUCTION

THE electrical and optical properties of zinc oxide have been the subject of a number of investigations.[1] In many respects zinc oxide stands somewhat between the heteropolar alkali halides and the homopolar semiconductors of the group IV elements, and it is often considered as an electronic semiconductor with a large energy gap (3.2 eV). Thus, replacement of zinc by an element of group I-A or I-B or of oxygen by an element of group V-A, should result in the formation of acceptor centers, while replacement of zinc by an element of group III-A or of oxygen by an element of group VII-A should lead to the formation of donor levels. Zinc vacancies and oxygen vacancies at the normal lattice sites should also act as acceptors and donors, respectively.

The electrical conduction so far observed, however, is exclusively of *n* type, and has been ascribed, depending upon the method of preparation, to a stoichiometric excess of zinc,[2] interstitial hydrogen,[3] substitutional indium,[4] and interstitial lithium.[5] The excess zinc might exist in interstitial positions as well as in the form of oxygen vacancies, and the both forms have been proposed.[1] On the other hand, it is also well known that the observed *n*-type conductivity of ZnO can be reduced by the incorporation of monovalent cations such as Li^+ or Cu^+,[6,7] in parallel with the idea that a group-I element substituting for zinc give rise to an acceptor level.

Electron spin resonance of donor centers in ZnO has been reported by Schneider and Raüber.[8] They observed a photosensitive signal with $g\cong1.955$ using a single crystal of ZnO that had been heated in vacuum with Zn metal. No interpretation regarding the structure of the defect responsible for this signal has yet been presented. We shall call this center the ZnO-*B* center for a reason to be made clear later. Judging from the treatment employed, the ZnO-*B* center is most likely either an interstitial zinc atom or an oxygen vacancy. This signal is observable, though much weaker, even at room temperature, implying that the level is deep (at least a few tenths of an eV below the conduction band). Schneider and Raüber also examined the effect on this signal of heating the single crystal of ZnO in hydrogen atmosphere, and found very little effect. This result is not surprising since hydrogen is known to occupy an interstitial position and acts as a relatively shallow donor (0.04 eV below the conduction band).[9] It would be quite interesting therefore to investigate the effect on the ZnO-*B* signal of introducing acceptor levels, and, if possible, to investigate the resonance signal of the acceptor centers also. The detection as well as the analysis of the resonance signal due to Li acceptor levels and the effect of introducing such acceptor levels upon the ZnO-*B* signals are reported in this paper.

The electron spin resonance spectrometer used in this investigation is a Varian Model V-4500 equipped with a 100-kc/sec modulation unit. The resonance cavity employed operates on the TE_{012} mode and has a slotted window at one end to permit direct illumination of the sample. The resonant frequency of the loaded cavity was in the range of 9150–9160 Mc/sec.

The ZnO samples used in this series of work were all in polycrystalline form. They were prepared by heating finely powdered ZnO at 900°C for 2 h. Donors and acceptors were introduced by adding to the ZnO powder aqueous solution of alkali halide or nitrate of an appropriate kind before the heating. Samples thus prepared all gave bright orange or green luminescence at 77°K under 3650 Å uv excitation.

II. POWDER PATTERN ANALYSIS

A phenomenological spin Hamiltonian for a para-

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[1] For a comprehensive review article on this subject, see: G. Heiland, E. Mollwo and F. Stöckmann, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 8, p. 191.

[2] D. G. Thomas, J. Phys. Chem. Solids **3**, 229 (1957).

[3] E. Mollwo, Z. Physik **138**, 478 (1954).

[4] D. G. Thomas, J. Phys. Chem. Solids **9**, 31 (1959).

[5] J. J. Lander, J. Phys. Chem. Solids **15**, 324 (1960).

[6] K. Hauffe and A. L. Vierk, Z. Physik. Chem. **196**, 160 (1950).

[7] C. Bogner and E. Mollwo, J. Phys. Chem. Solids **6**, 136 (1958).

[8] J. Schneider and A. Raüber, Z. Naturforsch. **16a**, 712 (1961).

[9] D. G. Thomas and J. J. Lander, J. Chem. Phys. **25**, 1136 (1956).

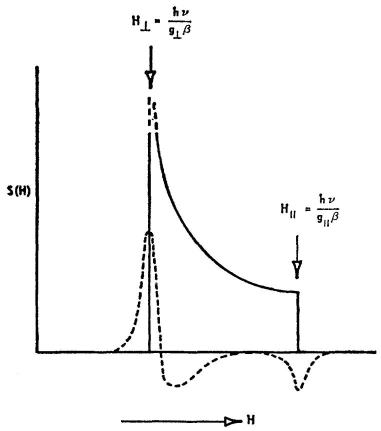

FIG. 1. The shape function $S(H)$ and the derivative curve of the spin resonance absorption expected from polycrystalline sample with $g_\perp > g_\parallel$.

magnetic center having an electron spin $S=\frac{1}{2}$ and a nuclear spin I is

$$\mathcal{H}=\beta\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{H}+\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}. \tag{1}$$

The first term represents the direct interaction of the electron spin and the applied magnetic field H, and the second term gives the hyperfine interaction between the electron spin and the nuclear spin.[10] For centers having axial symmetry, (1) can be written as

$$\mathcal{H}=\beta[g_\parallel S_zH_z+g_\perp(S_xH_x+S_yH_y)] +A_\parallel S_zI_z+A_\perp(S_xI_x+S_yH_y), \tag{2}$$

and the resonance condition with the applied microwave field $h\nu$ is met when

$$h\nu=g\beta H+Am, \tag{3}$$

where

$$g=(g_\parallel^2\cos^2\theta+g_\perp^2\sin^2\theta)^{1/2},$$

and

$$A=(A_\parallel^2g_\parallel^2\cos^2\theta+A_\perp^2g_\perp^2\sin^2\theta)^{1/2}/g.$$

θ is the angle between the symmetry axis and the magnetic field, and m is the magnetic quantum number of the nuclear spin I. It has been shown by many authors[11–15] that, if the spreading due to the anisotropy of the g tensor or the hyperfine interaction is significantly larger than the linewidth expected for a single crystal, the paramagnetic resonance absorption curve of a polycrystalline sample can be approximated by a so-called shape function

$$S(H)=\sin\theta\,|d\theta/dH|, \tag{4}$$

which can be evaluated analytically from (3). A schematic representation of such a shape function is given in Fig. 1 for the special case of $g_\perp>g_\parallel$ and $A=0$. The dashed line in Fig. 1 is the first derivative curve of the absorption spectrum anticipated from such a shape function. Thus, it is an easy matter to derive the g values in (2) from the characteristic shapes and the signs of the two strong signals observed at the points corresponding to $\theta=0$ and 90° of the derivative curve.[16] The effect of the hyperfine interaction upon the powder pattern is to split each of these signals into $2I+1$ equally spaced components, the spacings being $A_\parallel/(g_\parallel\beta)$ and $A_\perp/(g_\perp\beta)$, respectively.[17]

III. SPIN RESONANCE OF Li ACCEPTORS

ZnO powder fired with 10^{-3} (mole ratio) LiCl ordinarily shows no electron spin resonance signal either at room temperature or at 77°K. At 77°K, however, when the sample was illuminated with 3650 Å light obtained from AH-4 lamp coupled with Corning's 7-37 filter, a resonance signal with rather characteristic shape was obtained (Fig. 2). One can immediately recognize that the signal arises from the centers involving a nucleus with $I=\frac{3}{2}$ and having g and A tensors both of which are anisotropic. Also, the fact that the observed g value is larger than the value expected for a free-electron spin indicates that the signal arises from a hole rather than an electron. Once created, this signal is stable at 77°K. It can be quenched easily, however, simply by warming the sample up to room temperature, or even at 77°K by illuminating the sample with visible light of longer wavelength ($0.5\sim0.8\,\mu$). The only possible nuclei with $I=\frac{3}{2}$ in this sample are Cl^{35} (natural abundance 75%), Cl^{37} (25%), and Li^{7} (93%). Halide ions are large and, hence, unlikely to occupy interstitial sites. Also, substitutional halide ions are expected to behave as donors. On the other hand, lithium is well

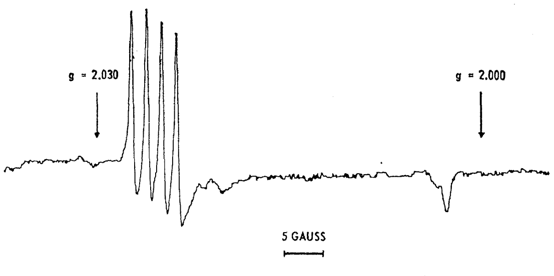

FIG. 2. Electron spin resonance signal obtained from ZnO:10^{-3} LiCl at 77°K under uv excitation.

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[10] The possible interaction involving the nuclear quadrupole moment and the interaction of the nuclear spin with the applied magnetic field is assumed to be small and are neglected in this expression. For a comprehensive discussion of the spin Hamiltonian, the reader is referred to B. Bleaney and K. W. H. Stevens, *Reports on Progress in Physics* (The Physical Society, London, 1953), Vol. 16, p. 108.

[11] R. H. Sands, Phys. Rev. **99**, 1222 (1955).

[12] J. W. Searl, R. S. Smith, and S. J. Wyard, Proc. Phys. Soc. (London) **74**, 491 (1959).

[13] F. K. Kneubüll, J. Chem. Phys. **33**, 1074 (1960).

[14] R. Neiman and D. Kivelson, J. Chem. Phys. **35**, 156 (1961).

[15] H. R. Gersmann and J. D. Swalen, J. Chem. Phys. **36**, 3221 (1962).

[16] Most of the experimental results so far reported on the analysis of the powder pattern are limited to materials in the vitreous state. The accuracy and reliability of such analysis extended to a polycrystalline material is well demonstrated in the work of P. H. Kasai and Y. Otomo, J. Chem. Phys. **37**, 1263 (1962).

[17] Signals corresponding to θ values other than 0° and 90° can occur if the components of the g and A tensors are specially related (see references 14 and 15). This point is omitted here since no such special effect is encountered in the present investigation.

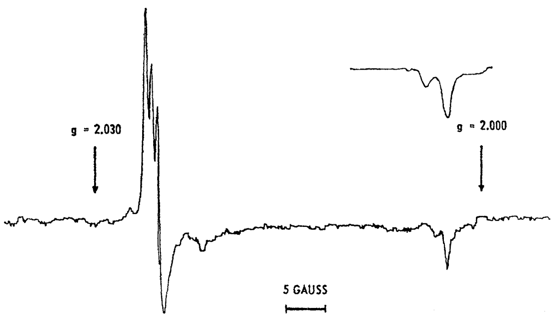

FIG. 3. Electron spin resonance signal obtained from ZnO:10^{-3} Li^6Cl (90% enriched) at 77°K under uv excitation. The figure at the upper right corner shows the high-field signal ($\theta=0$) of the same spectrum obtained at slower sweep rate. Note a doublet pattern of the signal.

known to act as acceptors in ZnO.[6] One can, therefore, conclude the following:

(1) The signal is due to holes captured at the Li acceptor levels.

(2) Illumination of the sample with uv light results in transferring an electron from a filled Li acceptor to a certain donor center which apparently constitutes a fairly deep electron trap at 77°K. A hole is, thus, created at the Li acceptor.

(3) Raising the temperature of the sample or illuminating it with visible light at 77°K results in recombination of these holes and the electrons.

That the Li acceptor is responsible for the signal is conclusively demonstrated by the spectrum (Fig. 3) obtained from a sample prepared by firing ZnO with 10^{-3} Li^6Cl (90% enriched). For Li^6 the nuclear spin is $I=1$ and the magnetic moment is $\mu=0.82$ (in nuclear magnetons), as compared to $I=\frac{3}{2}$ and $\mu=3.26$ for Li^7.

The measured values of the parameters in the spin Hamiltonian (2) are

$$\begin{aligned} g_{\parallel}&=2.0026\pm0.0005,\\ g_{\perp}&=2.0254\pm0.0005,\\ A_{\parallel}\ (\text{with }Li^7)&\leqq 0.1\times10^{-4}\ \text{cm}^{-1},\\ A_{\perp}\ (\text{with }Li^7)&=(1.73\pm0.02)\times10^{-4}\ \text{cm}^{-1}.\end{aligned} \tag{5}$$

The upper limiting value for $A_{\parallel}$ was estimated from the difference in the apparent widths of the high-field signals ($\theta=0$) of the Li^6 and Li^7 samples.

The crystal structure of ZnO is hexagonal (wurtzite type) and the basic arrangement of atoms is tetrahedral. The actual environment about each ion, however, is not exactly tetrahedral in its symmetry. Instead the interatomic distance between the nearest ions along the hexagonal axis is slightly shorter (1.96 Å) than those in the other three directions (1.98 Å). If we adopt a completely ionic model, the conduction band and the valence band of ZnO may be represented by the valence orbitals of Zn^{++} ions and O^{--} ions, respectively. Let us assume further that the orbitals of each ion are directed toward its four neighboring ions through sp^3 hybridization but without any significant overlap with the orbitals of these ions. Under these approximations we shall examine the Li acceptor level in ZnO. Because of the large ionization energy of the helium-like Li^+ ion, a hole bound at an Li acceptor site is least expected to become involved with the 1s orbital of Li itself. One is then led to assume that the hole is either shared among the four orbitals of the four oxygen ions surrounding the Li^+ ion, or completely localized, through a polarization process, in one of these four orbitals.[18] One must recall here that the observed value for $g_{\parallel}$ is almost exactly equal to the free-electron value. This fact strongly favors the latter model. Let us adopt this model, and denote the orbital of the nearest oxygen directed toward the lithium by ϕ_0 and the three other orbitals of the same oxygen but directed away from the lithium by ϕ_1, ϕ_2, and ϕ_3. These are then all sp^3 hybridized orbitals of the form

$$\phi_n=\tfrac{1}{2}\psi_{2s}+(\sqrt{3}/2)\psi_{2pn}, \tag{6}$$

where ψ_{2s} is the 2s atomic orbital of oxygen and ψ_{2pn} is the 2p atomic orbital of oxygen directed toward the respective direction. Then the ground-state wave function Φ_0 of the hole is simply

$$\Phi_0=\phi_0. \tag{7}$$

It has been shown that a deviation of the g tensor from the free-electron value is caused by the spin-orbit interaction of the form $\lambda\mathbf{L}\cdot\mathbf{S}$, and to a first-order approximation the shift is given by[19]

$$\begin{aligned}\Delta g_{ij}&=-\lambda\Lambda_{ij},\\ \Lambda_{ij}&=\sum_n\frac{\langle 0|L_i|n\rangle\langle n|L_j|0\rangle}{E_n-E_0},\end{aligned} \tag{8}$$

where $|0\rangle$ is the ground-state wave function of the center being considered, and the summation n includes all the excited states. In the principal axis system of the center having axial symmetry the tensor Λ is diagonal, the diagonal elements being $\Lambda_{zz}=\Lambda_{\parallel}$ and $\Lambda_{xx}=\Lambda_{yy}=\Lambda_{\perp}$. In our completely ionic model the most significant excited states are those in which the hole has been transferred into one of the three orbitals of the same oxygen directed away from the Li^+ ion. When one considers such excited states only, (8) becomes

$$\begin{aligned}\Lambda_{ii}&=\sum_{n=1}^{3}\frac{\langle\phi_0|L_i|\phi_n\rangle\langle\phi_n|L_i|\phi_0\rangle}{\Delta E}\\ &=\frac{\langle\phi_0|L_i^2|\phi_0\rangle}{\Delta E},\end{aligned} \tag{9}$$

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[18] Electron trapped in a nitrogen donor in diamond is completely localized in such a manner. W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, Phys. Rev. **115**, 1546 (1959).

[19] M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950).

which, combined with (6), immediately gives

$$\Delta g_{\parallel}=0,$$
$$\Delta g_{\perp}=-3\lambda/2\Delta E. \tag{10}$$

Since we are dealing with a hole, the sign of λ is negative. Though no spectroscopic data are available for O^-, the magnitude of its λ may be extrapolated from the atomic energies of the isoelectronic sequence of F, Ne^+, Na^{++}, etc.,[20] the result being $|\lambda|=0.014$ eV. The magnitude of ΔE is also not known. What primarily attracts the hole in the orbital ϕ_0 is the effective negative charge of $-e$ associated with monovalent Li^+ ion occupying a site for divalent Zn^{++} ion. ΔE, therefore, may be estimated to be around $e^2/(kd)$ where k is the dielectric constant of ZnO and d is the interatomic distance. Taking $k=8.5$[1] and $d=2.0$ Å, one then obtains $\Delta E\cong 0.85$ eV. Substitution of these values into (10) yields

$$\Delta g_{\parallel}=0;\quad \Delta g_{\perp}=+0.025.$$

The observed deviations are $\Delta g_{\parallel}=0.000$ and $\Delta g_{\perp}=+0.023$. Thus, one can see that the g tensor calculated according to the proposed model is in good agreement with the experimental result. It is not possible to demonstrate conclusively from this powder pattern analysis whether the hole is preferentially localized in the orbital directed along the symmetry axis of the crystal or in one of the three other orbitals. We believe that any one of the four orbitals is capable of capturing a hole because (a) the difference of 0.02 Å in the interatomic distances along the crystal symmetry axis and the other directions seems too small to cause such selection, and (b) the high-field signal always appears as a doublet with relative intensity ratio of 1:3 (Fig. 3).[20a]

The hyperfine interaction parameters $A_{\parallel}$ and $A_{\perp}$ can be shown to be[21]

$$A_{\parallel}=g_e\beta_e g_n\beta_n(P+2Q),$$
$$A_{\perp}=g_e\beta_e g_n\beta_n(P-Q), \tag{11}$$

where

$$P=(8\pi/3)|\psi(0)|^2,$$
$$Q=\langle[z^2-\tfrac{1}{2}(x^2+y^2)]/r^5\rangle.$$

The first term in (11) is the contact term while the second term represents the dipole-dipole term. Then from the observed hyperfine interaction with the Li^7 nucleus, one obtains

$$P=-2Q\cong\pm 0.11\times 10^{24}\ \text{cm}^{-3}.$$

Though distinct, these values are extremely small, and any quantitative calculation of them for our crude model could hardly be fruitful. It might be added, however, that a calculation based on a simple Slater orbital for ϕ_0 yielded a positive sign and the correct order of magnitude for the dipole-dipole term Q, while the contact term calculated from this orbital was not only too small but of the same sign. We believe that in this case the actual contact term arises predominantly from the polarization of the lithium $1s$ electrons by the paramagnetic hole. A reversal of sign for the contact term is known to be possible for such case.[22,23]

IV. SPIN RESONANCE OF THE ZnO-*B* CENTER

As mentioned earlier, a spin resonance signal arising from certain donors in ZnO had been detected by Schneider and Raüber at around $g\cong 1.96$.[8] Because they have reported only the value of $g_{\perp}$ from their work with single crystals at 77°K, and also because they have reported a rather wide scattering in the g values of the powder samples, this signal was re-examined in detail.

Figure 4 shows the electron spin resonance spectrum at $g\cong 1.96$ as obtained at 77°K with ZnO powder that had been heated in air at 900°C without any additive. Prior to the heating the same powder showed only a trace of such signal. As one can recognize, this signal also shows the pattern expected from centers having an anisotropic g tensor, although the observed anisotropy is much smaller than for the Li acceptor centers. The g values measured from this powder pattern at 77°K are

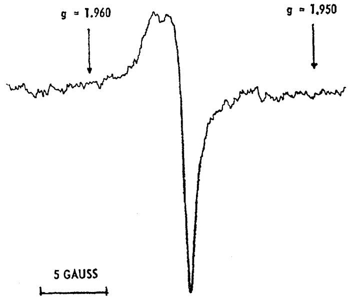

FIG. 4. Electron spin resonance spectra of the $g\cong 1.96$ region obtained at 77°K without uv illumination from pure ZnO powder that had been fired in air at 900°C.

$$g_{\parallel}=1.957\pm 0.001,$$
$$g_{\perp}=1.956\pm 0.001,$$
$$g_{\parallel}-g_{\perp}=0.0013\pm 0.0003.$$

The value of $g_{\perp}$ is in good agreement with the value reported previously from the single crystal work.[8] With this sample the signal appears to its fullest intensity without any uv illumination, and simultaneous illumination even seems to result in a slight decrease in intensity. Heating above 200°C and then quenching to 77°K had no effect on the intensity of this signal. Also as reported by Schneider and Raüber,[8] this signal is observ-

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[20] *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standard Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

[20a] *Note added in proof.* Recently Schneider and Schirmer reported on an ESR study of the Li acceptor centers in ZnO single crystals. They have found that, although all four orbitals surrounding a Li^+ ion are capable of capturing a hole, the predominant signal has axial symmetry along the c axis. The one-to-three intensity ratio of the observed doublet must then be interpreted as indicating that the specific probability for capture of a hole is nine times as great for an axial oxygen as for equatorial oxygen. See J. Schneider and O. Schirmer, Z. Naturforsch. **18a**, 20 (1963).

[21] See for example, reference 18.

[22] J. H. Wood and G. W. Pratt, Phys. Rev. **107**, 995 (1957).

[23] V. Heine, Phys. Rev. **107**, 1002 (1957).

able even at room temperature, though its intensity is weaker by a factor of 50 or more.

In the absence of any foreign material, the most likely defects that can act as donors in ZnO are oxygen vacancies and interstitial zinc. We have concluded that oxygen vacancies are responsible for the observed signal on the bases of the following series of observations:

(a) The intensity of this signal is greatly enhanced (by a factor of 10) if the sample has been fired in a reducing condition (fired in H_2 or fired with 1% of ZnS in an inert atmosphere).

(b) Firing at comparatively high temperature (~900°C) is necessary in order to create this center. Interstitial zinc is known to diffuse at much lower temperature ($<500°$).[2]

(c) Heating a sample at around 500°C for a few minutes in air is known to remove most of the interstitial zinc.[2] Annealing of our sample at 500°C in air produced no effect upon the signal.

(d) If the signal is due to interstitial zinc, this zinc must exist as Zn^+ ion. Then the electron responsible for the signal must be well localized in the vicinity of the interstitial zinc ion (the second ionization of interstitial zinc does not take place at least up to 750°C)[2] and one would expect to observe the hyperfine satellites due to Zn^{67} ($I=\frac{5}{2}$, natural abundance 4.1%). The intensity of the main signal is such that the observation of such hyperfine components should be possible if they indeed exist. No such satellites were observed. If the donors were oxygen vacancies, instead, and the paramagnetic electrons were shared among the orbitals of surrounding zinc ions, reduction of the hyperfine spreading to within the width of the observed signal would not be entirely unexpected.

(e) As will be shown below, the g value calculated on the basis of the oxygen vacancy model is in fair agreement with the observed value.

A similar signal had been detected in ZnS at $g=1.88$. It was called the ZnS-B signal and was attributed to donor levels created by sulfur vacancies.[16] Let us examine the g value of the "ZnO-B" center under the proposed model and under the same approximation used for the calculation of the g tensor of the Li acceptors. Neglecting the slight deviation from exact tetrahedral symmetry, we will assume that the electron in a ZnO-B center is shared equally among the four valence orbitals of the surrounding zinc ions directed toward the vacancy. Then the ground-state function Φ_0 of the center may be written as

$$\Phi_0=\tfrac{1}{2}\sum_{i=1}^{4}\phi_0(\mathrm{Zn}_i). \qquad (12)$$

$\phi_0(\mathrm{Zn}_i)$ is the sp^3 hybridized valence orbital of the ith zinc ion directed toward the vacancy. No anisotropy of the g tensor is expected from a wave function of this form. Again only the orbitals of these four ions that are directed away from the vacancy will be considered for the excited states. Let $\phi_n(\mathrm{Zn}_j)$ represent one of such excited states associated with the jth ion. We also use further approximations of the type

$$\begin{aligned}\langle\Phi_0|L_z|\phi_n(\mathrm{Zn}_j)\rangle&=\frac{1}{2}\left\langle\sum_{i=1}^{4}\phi_0(\mathrm{Zn}_i)\,|L_z|\phi_n(\mathrm{Zn}_j)\right\rangle\\&=\tfrac{1}{2}\langle\phi_0(\mathrm{Zn}_j)|L_z|\phi_n(\mathrm{Zn}_j)\rangle.\end{aligned} \qquad (13)$$

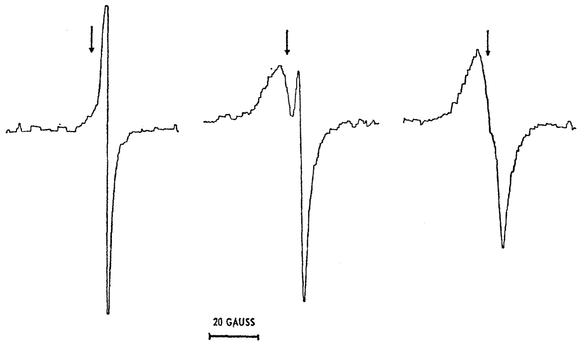
A calculation entirely analogous to that performed on the Li acceptor center then yields

$$\begin{aligned}\Delta g&=-\frac{\lambda}{2\Delta E}\sum_{i=1}^{4}\langle\phi_0(\mathrm{Zn}_i)|L_z^2|\phi_0(\mathrm{Zn}_i)\rangle,\\&=-\lambda/\Delta E.\end{aligned} \qquad (14)$$

The last expression in (14) is obtained by noting that, if we identify the z axis with the crystal axis, one of the ϕ_0 orbitals is parallel to the z axis while the remaining three ϕ_0 orbitals all make an angle of $\sin^{-1}(8/9)^{1/2}$ with the z axis. Since we are concerned here with an electron excess center, the sign of λ is positive and its value was estimated from the atomic energy levels of Zn^+ ion to be 0.072 eV.[20] The value of ΔE is difficult to estimate. It has been said, however, that the recombination of holes with electrons at oxygen vacancies is responsible for the observed green luminescence (~2.4 eV) of ZnO.[24] Therefore, we will assume $\Delta E\cong 0.8$ eV. Substituting these values into (14), one obtains

$$\Delta g=-0.09.$$

In view of the crude approximations involved in the calculation, the agreement with the experimental result of $\Delta g=-0.05$ must be considered fair. Since the ground state of Zn^+ ion is $3d^{10}4s^1$, a complete sp^3 hybridization



(a) (b) (c)

FIG. 5. Electron spin resonance spectra of the $g\cong 1.96$ region obtained from (a) ZnO, (b) ZnO:10^{-2} NaCl, and (c) ZnO:10^{-1} NaCl at 77°K without uv illumination. The arrows indicate the points corresponding to $g=1.960$, and the field increases from left to right.

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[24] F. A. Kröger and H. J. Vink, J. Chem. Phys. **22**, 250 (1954).

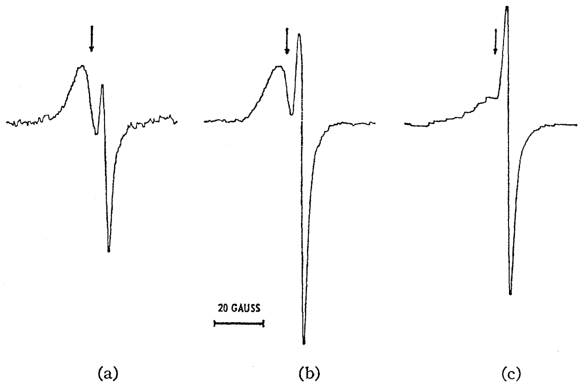

FIG. 6. Electron spin resonance signals of ZnO-B and ZnO-B' obtained from ZnO:10^{-2} NaCl at 77°K with three different microwave power levels: (a) 1 mW, (b) 4 mW, and (c) 16 mW. The relative settings of the amplifier gain were 4, 2.6, and 1 for the spectra (a), (b), and (c), respectively. The arrows indicate the points corresponding to $g=1.960$, and the field increases from left to right.

of valence orbital is hardly expected to take place. The ground-state wave function Φ_0 of the electron trapped in the ZnO-B center is then expected to have more s-type character than assumed in our calculation. Such consideration predicts that the true Δg must be smaller than the value calculated above. We should also note the experimental result $|\Delta g_\perp|>|\Delta g_{\|}|$. This may be interpreted as the consequence of the fact that, among the four orbitals in (12), the electron favors the orbital directed along the crystal axis slightly more than the others. This is to be expected since this orbital is slightly closer to the vacancy than the others are.

V. SPIN RESONANCE OF HALOGEN DONORS

Shown in Fig. 5 are the electron spin resonance spectra of the ZnO-B signal region obtained at 77°K without uv excitation from samples prepared by firing, respectively, (a) pure ZnO, (b) ZnO+10^{-2} NaCl, and (c) ZnO+10^{-1} NaCl at 900°C in air for 2 h. The spectrum (a) should, of course, be identical to that given in Fig. 4 and the apparent difference is due to the entirely different sweep rates of the magnetic field. One will immediately notice the gradual displacement of the sharp ZnO-B signal with a much broader resonance signal, say the ZnO-B' signal, with the increasing amount of NaCl used. The responses of the ZnO-B' signal to uv illumination, to illumination by visible light, and to raising the temperature of the sample were found to be almost identical with those of the ZnO-B signal. Since these two signals are so close to each other one may question whether they are really two independent signals: Spectra like (b) might be due merely to some distortion brought to the original ZnO-B centers, resulting in a larger anisotropy of the g tensor. The fact that the spectrum (b) is truly a superposition of two independent signals is clearly demonstrated in the following two figures, 6 and 7. Figure 6 shows the electron spin resonance of ZnO:10^{-2} NaCl taken at three different microwave power levels ($T=77$°K). It is apparent that the ZnO-B signal is associated with centers which suffer no significant saturation effect at 77°K, while the ZnO-B' signal is due to centers subjected to severe saturation. The ZnO-B signal was found to show saturation only above 50 mW. In view of this significant difference in the degree of saturation observed at 77°K, one might expect a somewhat opposite change in the relative intensities of these signals if the temperature of the sample were raised keeping the power level constant. This was indeed found to be the case as shown in Fig. 7. At 140°K the ZnO-B' signal appears isotropic and quite sharp ($\Delta H_{\text{peak-to-peak}}\cong 1.8$ G). Its g value measured at 140°K is

$$g=1.960\pm 0.001.$$

Thus, the ZnO-B' center is also a donor. The closeness of the g values of the ZnO-B and -B' centers, coupled with the fact that their ionization energies must also be within a close range, strongly suggests a similarity between the ground-state wave functions of these centers. The donor centers due to halogen substituting for oxygen could just meet these requirements. Again the trapped electron is shared only among the orbitals of the surrounding zinc ions. In order to prove that halogen ions are indeed involved in the ZnO-B' centers, two samples were prepared by firing ZnO:10^{-2} KCl and ZnO:10^{-2} KF. At 77°K both samples showed the broad ZnO-B' signal in addition to the sharp ZnO-B signal. At 180°K, however, the two samples showed distinctly different ZnO-B' signals (see Fig. 8). The ratio of the peak-to-peak separations of the two ZnO-B' signals in Fig. 8 is about 1/3.2 in close agreement with the ratio of the nuclear magnetic moments of chlorine and fluorine nuclei. The small hyperfine interaction with halogen nucleus is expected since the contact term P in (11) at the halogen nucleus must be small, and the dipole-dipole term Q must vanish by virtue of the symmetry of the wave function. Thus, the observed

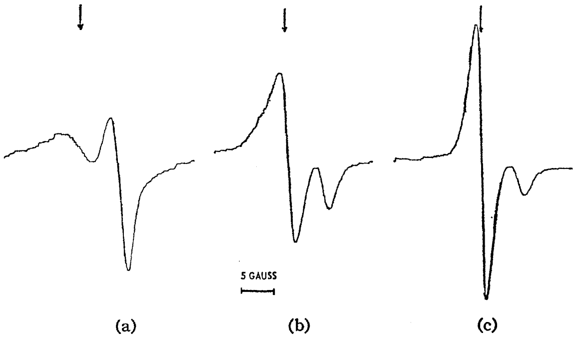

FIG. 7. Electron spin resonance signals of ZnO-B and ZnO-B' obtained from ZnO:10^{-2} NaCl at three different temperatures: (a) 77°K, (b) 110°K, and (c) 140°K. The power level was kept at 4 mW. The arrows indicate the points corresponding to $g=1.960$, and the field increases from left to right.

proportionality in the peak-to-peak separation permits one to estimate an upper limiting value for the contact term P, and one obtains $|\psi(0)|^2 \leqq 0.026 \times 10^{24}$ cm^{-3}.

A speculation that the ZnO-B' signal could be ascribed to the ZnO-B center with halogen in the near vicinity must be excluded on the following ground. There should be a repulsive force between the substitutional halogen ions and the oxygen vacancies both of which possess effective positive charge. No broadening effect was seen on the concurrently observed Li acceptor signal despite of the fact that an attraction is expected between the halogen donors and the Li acceptors.

We conclude, therefore, that the ZnO-B signal is due to oxygen vacancies and the ZnO-B' signal is due to substitutional halogen ions. Possible overlapping of ZnO-B and -B' signals could well explain the scattering of the g values reported by Schneider and Raüber on their powder samples.[8] Also it would be quite interesting to examine a possible parallelism between the erratic behavior of the signal due to the proximity of the ZnO-B and -B' centers and some of the irregular behaviors observed on ZnS-B signals.[25]

VI. RELATIONS FOR ZnO BETWEEN Li ACCEPTORS, ZnO-B AND -B' DONORS, LUMINESCENCE, AND THERMOLUMINESCENCE

One of the most striking effects of introducing lithium into zinc oxide is the weakening or, depending upon the amount of Li introduced, the complete disappearance of the ZnO-B and -B' signals. ZnO fired in air with 10^{-3} LiCl shows only a trace of signal at $g \cong 1.95$. This result should be compared with the spectrum (b) of Fig. 4 obtained from ZnO fired with 10^{-2} NaCl. We believe this is due to strong association of the Li centers, which have effective negative charge when they are ionized, with ionized donors having effective positive charge.

It is possible, however, to introduce both Li acceptors and ZnO-B or -B' centers either by carefully controlling the amount of Li to be added or by firing the material under a reducing condition. When this is done, the ZnO-B (or B') signal also become photosensitive. That is, if the ZnO-B (or B') signal is seen originally at 77°K without uv illumination, uv illumination of the sample at 77°K results in the appearance of the Li-acceptor signal and also an increase of the ZnO-B (or B') signal by an amount more or less proportional to the intensity of the newly appeared Li acceptor signal. Under the action of uv light, electrons must have been transferred from the filled Li acceptor levels into the ionized ZnO-B (or B') donor levels. An extreme example is ZnO fired with 10^{-2} LiNO$_3$ under a reducing condition. While this sample shows no electron spin resonance signal at all at 77°K without uv illuminations, strong signals of both the Li acceptors and the ZnO-B centers are obtained when excited by uv light. Compensation of the ZnO-B donors with the Li acceptors is apparently achieved to near completion in this particular sample.

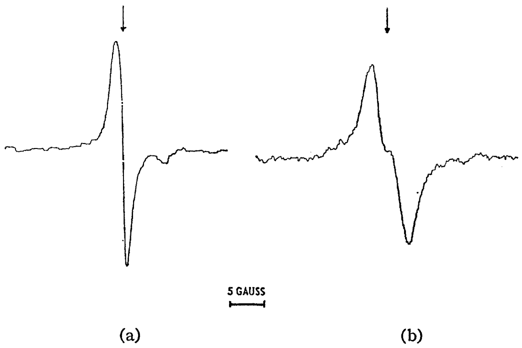

FIG. 8. Electron spin resonance signals of ZnO-B' centers obtained at 180°K from (a) ZnO:10^{-2} KCl and (b) ZnO:10^{-2} KF. The arrows indicate the points corresponding to $g = 1.960$, and the field increases from left to right.

It is well known that ZnO fired under reducing conditions gives off green luminescence under uv excitation, while ZnO fired in the presence of group III-A or VII-A element and under oxidizing conditions has orange or yellow luminescence.[24] The green luminescence has been ascribed to the recombination of holes in the valence band with electrons trapped at oxygen vacancies.[24] The orange band is likely to be associated with centers similar to those proposed for the self-activated luminescence of ZnS, namely, an association of a zinc vacancy and an ion of group III-A or VII-A element. In parallel with the model proposed for the green luminescence, it was found that the intensity of the green luminescence is proportional to the intensity of the ZnO-B signal (within the experimental accuracy), and has no apparent dependence upon the ZnO-B' signal. Electron spin resonance due to the luminescent centers of the orange band, however, has not yet been detected.[26]

The thermoluminescence of zinc oxide has been reported many times. Two main peaks are usually reported at 120 and 185°K.[1] Preliminary examination of our samples in this respect revealed that the first glow peak consists mostly of orange luminescence while the second peak is predominated by green luminescence. It was further found that the second peak occurs only for those samples which exhibit both the Li-acceptor and the ZnO-B signals. This can be understood easily if holes from the Li acceptors are released into the valence band. Thus, the sample showing only the ZnO-B signal and therefore strong green luminescence at 77°K under uv excitation produced hardly any thermoluminescence. Results of a more quantitative examination of the thermoluminescence, particularly in connection with the intensities of the ZnO-B, the ZnO-B' and the Li acceptor signals will be reported later.

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[25] Y. Otomo and P. H. Kasai (unpublished).

[26] Electron spin resonance due to similar centers in ZnS has been detected. See reference 16.