Notice that Eq. (15) applies equally to tetrahedral and octahedral molecules. Eq. (15) should replace Eq. (4.11) of Ref. [3]. With this result, the conclusion of DONG and BLOOM [2] that the best value for $|\Delta c|$ in the "equal correlation time approximation" is 18.2 kHz [16] rather than 21.0 kHz [11] is reconfirmed.

In the treatment presented here, the effect of centrifugal distortion on the relaxation of the nuclear magnetization has been completely disregarded. This can be done as long as the associated energy splitting $E_{\text{c.d.}}$ is collisionally quenched, i. e., if the condition

$$(1/\hbar)\, E_{\text{c.d.}} \ll \omega_{\text{coll}} \qquad (16)$$

is satisfied. Condition (16) imposes a lower limit on the pressures for which Eqs. (12) or (15) can be applied. Since $\omega_{\text{coll}} \approx 10^9$ Hz at 1 atm., and [11] $E_{\text{c.d.}}/\hbar \approx 10^7$ to 10^8 Hz for molecules such as CH_4, SiH_4, this lower pressure limit is of the order of 0.1 to 1.0 atm. (at room temperature). Certainly, then, the rôle of centrifugal distortion on NMR needs further theoretical clarification. Recent experiments [17] in CH_4 indicate that the influence of centrifugal distortion shows up below 0.5 atm. On the other hand, recent measurements [18] in CF_4, SiF_4, GeF_4, and SF_6 show that centrifugal distortion does not affect the nuclear spin relaxation down to about 0.01 atm.

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Defects in Neutron-irradiated ZnO (I)

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After irradiation with fast neutrons, several paramagnetic centers have been observed in ZnO by ESR. They result from electrons trapped at oxygen vacancies and from holes trapped at more complex defect associates.

After exposure to fast particle irradiation (e^-, n), various types of paramagnetic defect centers have been observed in ZnO single crystals by electron spin resonance (ESR). One prominent defect is the F^+-center, i. e. an electron trapped at an oxygen vacancy. An unambiguous identification of this center was made possible by the observation of hyperfine structure arising from the four Zn^{67}-ligands [1]. As in ZnS [2], we found that the F^+-center in ZnO can also be created by grinding single crystals. In contrast, heating in zinc vapour does not lead to a noticeable formation of F^+-centers, but to the incorporation of interstitial zinc into the ZnO lattice. ESR of trapped-hole centers has also been observed in ZnO crystals exposed to 3 MeV electrons [3] or to fast neutrons [4]. The paramagnetic centers were ascribed to holes trapped at zinc vacancies.

It is the purpose of this note to report additional investigations on these trapped-hole centers which make it appear rather unlikely that they arise from *isolated* zinc vacancies: Nominally pure ZnO single crystals, obtained from the 3M-Company, were irradiated to a dosage of 10^{17} fast neutrons/cm^2, at about 150 °C. To suppress activation, the samples were shielded by 1 mm Cd. Typical X-band ESR-spectra observed for such samples at 77 °K, and under $H \parallel c$ are shown in Fig. 1 a, b.

We first consider the signal labeled P in Fig. 1 b. It arises from a $S=1/2$ center having C_s-symmetry. The principal components of its $\boldsymbol{g}$-tensor are $g_1=2.0038(3)$, $g_2=2.0180\,(3)$ and $g_3=2.0191\,(3)$. The g_1-axis forms an angle of 69.3° with the c-axis. The g_3-axis is perpendicular to the center's mirror plane, spanned by the axial and one of the six non-axial bond directions in the ZnO lattice. Thus, the P-center might arise from holes trapped at one of the three non-axial oxygen ligands around a zinc vacancy, as already postulated before [3, 4].

However, no ESR signal arising from holes trapped at the axial oxygen ligand could be detected. This is surprising since previous ESR-studies of the deep acceptor center formed by substitutional Li^+ in ZnO and BeO have shown that this axial site is energetically strongly favoured [5]. This is also true for the isolated Be-vacancy in BeO [6]. Therefore, the P-center might arise from Zn−O divacancies, or even Zn−O−Zn trivacancies, both oriented along the c-axis.

Above 77 °K, motional effects were observed in the ESR-spectrum of the P-center. At room temperature, the spectrum has reached axial symmetry around the

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c-axis, with $g_{\parallel}=2.0149(5)$ and $g_{\perp}=2.0134(3)$. Thermally activated hopping of the hole among equivalent or, within the range of kT, almost equivalent oxygen sites must account for this averaging process. The value observed for $g_{\parallel}$ at 300 °K is definitely smaller than that observed for the P-center at 77 °K under $H \parallel c$, where $g_c=2.0162(3)$. This suggests that the hopping process may not be restricted to occur only between the three non-axial oxygen ligands around a zinc vacancy. Additional oxygen sites, within the range of kT, do not exist around an axial divacancy, but possibly around a linear, axial trivacancy. It should again be noted that the g-shifts of the thermally averaged P-center are not compatible with a hole rapidly hopping among the four oxygen ligands of an *isolated* metal site. In this case, a much smaller anisotropy $g_{\parallel}-g_{\perp}$ should result, as observed for the Li^+-center in BeO [5].

The signal labeled Q in Fig. 1 b also arises from a $S=1/2$ trapped-hole center, with

$$g_1=2.0038(3),\quad g_2=2.0182(3)\quad \text{and}\quad g_3=2.0217(3),$$

at 77 °K. Its symmetry is only C_1. The g_1-axis is tilted by about 10° from a non-axial bond direction. It is tempting to assign the Q-signal to centers resulting from non-axial ionic arrangements of a di- or trivacancy in the ZnO lattice.

Apart from the ESR-signal of the F^+-center, seen in Fig. 1 b, the signals labeled R, S and U still await further investigation. The symmetry of the S-center is lower than C_{3v}, with $g_c=2.0041(3)$. Its angular dependence occurs in a very narrow range of magnetic fields. The lines labeled U in Fig. 1 b arise from a low-symmetry $S=1$ center of unknown structure.

The prominent lines labeled T in Fig. 1 a have been investigated more in detail. They arise from a $S=1$ trapped-hole center having C_s-symmetry. The magnetic parameters of this triplet center were reported previously [3] and agree well with our results:

$$g_1=2.0095(5),\quad g_2=2.0141(5),\quad g_3=2.0190(5),$$
$$|D|=1465(5)\text{ MHz}\quad\text{and}\quad |E|=58(2)\text{ MHz},$$

at 77 °K. D and g_1 are measured along one of the six axes connecting nearest non-axial oxygen sites. The g_3-axis forms an angle of 52° with the c-axis. These data are compatible with holes trapped at two non-axial oxygen ligands around a zinc vacancy. However, the lack of corresponding $S=1$ centers formed by holes trapped at one axial and one non-axial oxygen site makes it again appear questionable that the center arises from an isolated zinc vacancy.

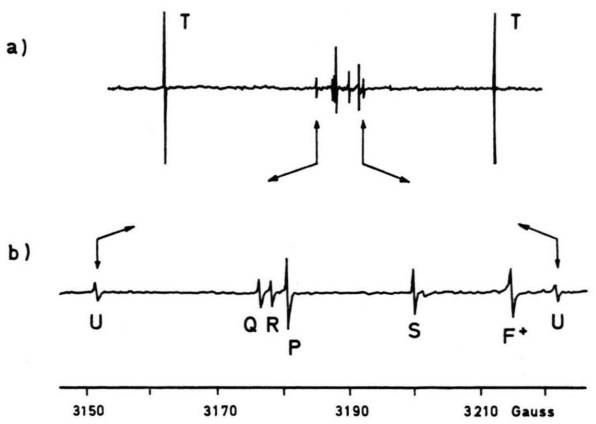

Fig. 1. ESR spectrum of a neutron-irradiated ZnO crystal recorded at 9.1 GHz, 77 °K and under $H \parallel c$. The magnetic field scan of the upper spectrum (a) is 10× that of the lower trace (b).

The ESR-signals of the T-center disappear above 100 °K. No motionally averaged ESR-spectra could be detected at elevated temperatures. At 77 °K, both T- and U-centers were completely quenched by illumination with the green 546 nm Hg-line. A slight increase of the intensity of the P- and Q-center lines was simultaneously observed. The question remains whether the T-center is a different charge state of the P-center.

To summarize we can state that fast particle irradiation of ZnO at room temperature and above can lead to the formation of isolated oxygen vacancies in fair concentration, as demonstrated by the ESR-detection of the F^+-center. In contrast, isolated zinc vacancies are probably mobile at room temperature and, consequently, tend to associate with oxygen vacancies — or with impurity ions in ZnO. Association of neutron-induced lattice defects with Fe^{3+} and Cu^{2+} ions will be reported in a forthcoming commmunication. In order to observe ESR of the isolated zinc vacancy in ZnO, fast particle irradiation at low temperature may be advisable.