

accurately expressed for all of these crystals by

$$1/T_1 = 5.1 \times 10^{-12} H^2 T + 7.8 \times 10^4 (T/210)^7 J_6(210/T), \quad (9)$$

where H is in Oe, T in $^\circ\text{K}$, and T_1 in sec. The two terms in this expression, identified with the direct and Raman processes, are consistent with the model in which the only effective relaxation is by means of the hyperfine interaction of an isolated F center with the surrounding nuclei and in which the lattice phonons are described

by a Debye distribution with the same cutoff as has been determined from measurements of specific heat.

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Concentration-Dependent Electron Spin Resonance*

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A number of workers have studied the decrease of the intensity of a nuclear magnetic resonance (NMR) line as one adds impurities to the specimen. Usually the intensity of the line is $\propto (1-c)^n$, where c = the concentration of the impurities and n is the so-called wipe-out number, i.e., if the impurity is within a sphere containing n neighboring positions its effect is large enough so as to cause a nuclear quadrupole splitting of the host nuclei so that they no longer contribute to the NMR line. Experimentally one can determine n . The extension of this type of experiment into the domain of electron spin resonance (ESR), in a very simple way, is described. Also, the wipe-out number for Mn^{2+} in two systems, $(\text{Zn}_{1-c} + \text{Cd}_c)\text{S}$ and $\text{Zn}(\text{S}_{1-c} + \text{Se}_c)$, is measured. One finds $n = 157$ and 270, respectively.

INTRODUCTION

In the early studies of the nuclear magnetic resonance (NMR) of metals and alloys, Bloembergen and Rowland¹ measured the decrease of intensity of the Cu NMR in the cubic system $\text{Cu}_{1-c} + \text{Zn}_c$ as c increased. They found that the intensity, I , of the Cu NMR decreased with the concentration c of Zn according to

$$I = I_0(1-c)^n, \quad (1)$$

where n is the so-called wipe-out number or dead-site number. Equation (1) comes from the assumption that if a given Cu nucleus has a Zn atom in any one of n neighboring positions, the resultant nuclear quadrupole resonance (NQR) splitting will be large enough so that the Cu nucleus no longer contributes to the NMR line. By measuring I versus c , one can determine n for the system in question. Cu has a nuclear spin of $\frac{3}{2}$ which in a magnetic field splits into four equally spaced levels. The transitions between the $\pm\frac{1}{2}$ and $\mp\frac{1}{2}$ levels will be unaffected to first order by quadrupole effects.² On the

other hand, the transitions from the $\pm\frac{3}{2}$ to $\pm\frac{1}{2}$ levels will be affected by first-order quadrupole effects. Thus, one can measure the wipe-out number for either the first- or second-order effects.^{1,3} A number of these experiments have been performed in metals.⁴ The major contribution to n in metals appears to arise from long-range oscillations in the electron charge density around the solute atom.⁵

This type of experiment has also been carried out in a number of cubic alkali-halide systems.⁶ For example, the wipe-out number for either the Na or Cl in the system $\text{Na}(\text{Cl}_{1-c} + \text{Br}_c)$ can be studied. It appears that one can do a reasonable job in calculating the wipe-out numbers by focusing one's attention on the dipole moments, direct and induced, that occur due to the strain in the lattice set up by the solute atom.^{7,8}

An experiment similar to the above type has been performed on⁹ single crystals of $(\text{Na}_{1-c} + \text{Ag}_c)\text{NO}_3$. In this

³ T. J. Rowland, *Acta Met.* **3**, 74 (1955).

⁴ T. J. Rowland, *Phys. Rev.* **119**, 900 (1960).

⁵ W. Kohn and S. H. Vosko, *Phys. Rev.* **119**, 912 (1960).

⁶ H. Kawamura, E. Otsuka, and K. Ishiwatari, *J. Phys. Soc. Japan* **11**, 1064 (1956); E. Otsuka and H. Kawamura, *ibid.* **12**, 1071 (1957); E. Otsuka, *ibid.* **13**, 1155 (1958); E. Otsuka, Y. Oshio, T. Kobayashi, and H. Kawamura, *ibid.* **14**, 1454 (1959); Y. Fukai, *ibid.* **18**, 1580 (1963).

⁷ T. P. Das and B. G. Dick, *Phys. Rev.* **127**, 1063 (1962).

⁸ Y. Fukui, *J. Phys. Soc. Japan* **18**, 1580 (1963).

⁹ M. I. Kornfeld and V. V. Lemanov, *Zh. Eksperim. i Teor. Fiz.* **39**, 53 (1960) [English transl.: *Soviet Phys.—JETP* **12**, 38 (1961)].

* A preliminary account of some of this work has appeared: G. Burns, *Bull. Am. Phys. Soc.* **7**, 199 (1962).

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¹ N. Bloembergen and T. J. Rowland, *Acta Met.* **1**, 731 (1953).

² For general references to the field of NQR see: M. C. Cohen and F. Reif, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 5; and T. P. Das and E. L. Hahn, *ibid.*, Suppl. 1.

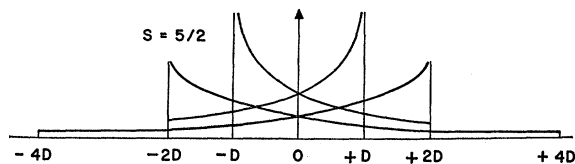


FIG. 1. The resultant powder pattern for absorption versus field for a spin Hamiltonian of the form of the first two terms in Eq. (2) for $S = \frac{5}{2}$ to first order in D . The 0 really corresponds to the $\pm\frac{1}{2} \leftrightarrow \mp\frac{1}{2}$ transitions which are undisplaced to first order in D . Thus, the 0 corresponds to the magnetic field of ≈ 3400 G for a 3-cm spectrometer and $g = 2.00$.

crystal, which is noncubic, one has a value of the nuclear quadrupole coupling constant, eQq/h , large enough so that three resonant absorptions are observed in an NMR experiment. The central line is due to transitions $\pm\frac{1}{2}$ to $\mp\frac{1}{2}$, which is undisplaced to first order in eQq/h . The satellites are due to transitions $\pm\frac{3}{2}$ to $\pm\frac{1}{2}$. These satellites are affected by the concentration of Ag atoms to first order. A value of $n = 138$ was obtained.⁹

The other type of experiment, closely related to the above types, is a pure quadrupole resonance experiment. For example, the NQR of Cl in solid solutions of parahalogenobenzenes has been observed and wipe-out numbers obtained.¹⁰

The purpose of this paper is twofold. First, it shows how to extend this type of experiment into the domain of electron spin resonance (ESR) in a very simple way. Second, values of the wipe-out numbers are measured in the hexagonal ZnS system.

EXPERIMENTAL PART

To do the experiment, a small amount (0.05 mole%) of Mn^{2+} was added to ZnS, and the ESR of the Mn^{2+} was measured at room temperature in the two systems $(Zn_{1-c} + Cd_c)S$ and $Zn(S_{1-c} + Se_c)$. One could in principle use single crystals of these compounds for the measurements. One would have to grow the crystals with Mn^{2+} and various percentages of Cd, or Se; make the intensity measurements; compensate for the various sample sizes; then analyze for the concentrations of Mn and Cd, or Se. This would be difficult because the crystals would be small and the concentrations of Mn are small. Also it is chemically difficult to separate Cd from Zn just as it is difficult to separate Se from S.

Rather than using single crystals for the measurements it was decided to use powders. The use of powders, and solid-state reactions to form the various mixed systems, eliminates the difficulties mentioned. The powders were formed by mixing the appropriate amount of CdS (or ZnSe) with ZnS and adding the Mn in the form of $MnSO_4$ in solution. Adding the Mn in water solution helps to spread it evenly throughout the ZnS powder. The $(Zn_{1-c} + Cd_c)S$ system was then dried, mixed and fired at $700^\circ C$ for ≈ 1 h in flowing H_2S gas.

¹⁰ For a review of this work, see G. Boudouris, J. Phys. Radium 23, 43 (1962).

This latter step serves to get rid of the oxygen from the $MnSO_4$. The powder was then reground and refined. Then the powder was pressed into pellets and fired in vacuum for ≈ 16 h at $1100^\circ C$.

The $Zn(S_{1-c} + Se_c)$ was made by adding the $MnSO_4$ to the appropriate amount of ZnS and firing it in flowing H_2S gas at $700^\circ C$ for ≈ 1 h. Then the ZnSe was mixed and the powder refired in He gas at $700^\circ C$ and remixed and refired. Then pellets were pressed out and fired in vacuum for ≈ 16 h at $1100^\circ C$. Weight loss, ESR, and x-ray measurements at various stages of the process indicated there was no loss of material and the final result was the hexagonal phase of ZnS with the appropriate lattice constants, which depend on c .

The spectra of Mn^{2+} in the hexagonal phase of¹¹ ZnS can be fitted by the spin Hamiltonian¹²

$$H = g\beta\mathbf{H} \cdot \mathbf{S} + D[S_z^2 - \frac{1}{3}S(S+1)] + (F/180)[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2] + A\mathbf{I} \cdot \mathbf{S}, \quad (2)$$

with¹¹ $g = 2.0016$, $D = -113$ G, $F = -8$ G, $A = -70$ G. Since the F term has relatively little effect on the spectra and the hyperfine term $(A\mathbf{I} \cdot \mathbf{S})$ is isotropic, one can, for

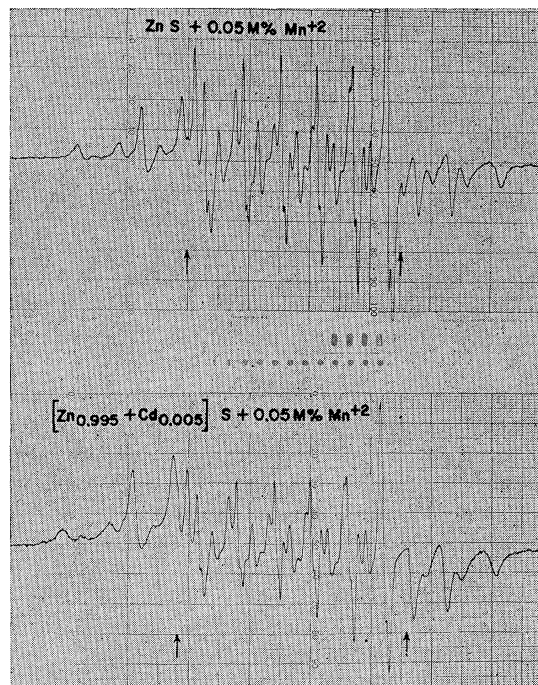


FIG. 2. The ESR of Mn^{2+} in two samples. The lines are described in detail in the text. The spectra were taken at room temperature using a 3-cm spectrometer. Between the arrows on the top spectrum the gain was reduced by a factor of 0.41 and on the bottom spectrum by a factor of 0.13.

¹¹ S. P. Keller, I. L. Gelles, and W. V. Smith, Phys. Rev. 110, 850 (1958).

¹² For general references to the field of ESR, see B. Bleaney and K. W. H. Stevens, Rept. Progr. Phys. 16, 108 (1953), and W. Low, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Suppl. 2.

a first approximation, consider the effect of the first two terms in the spin Hamiltonian in a powder. As has been pointed out previously,¹³ the first two terms in Eq. (2) are formally the same as the nuclear case where one is doing a nuclear-magnetic-resonance experiment with a nuclear quadrupole splitting. Thus, to first order in the parameter D the results of Feld and Lamb¹⁴ apply. Figure 1 shows the powder pattern for $S = \frac{5}{2}$. The higher order effects do not alter the results shown in Fig. 1 appreciably¹³ since one still has the very strong absorptions due to crystallites with $\theta = \frac{1}{2}\pi$ ($\theta =$ the angle between the external field and the crystal c axis) and a discontinuity in the absorption due to crystallites with $\theta = 0$. The positions are only shifted slightly by second-order corrections, i.e., $\pm 2D \mp D^2/\nu_0$ and $\pm D \pm 5D^2/4\nu_0$, where $\nu_0 = 3400$ G for a 3-cm spectrometer and $g = 2$. The hyperfine term will have a big, but isotropic, effect on the spectra because A is large. Since the nucleus has a spin, $I = \frac{5}{2}$, each line in the powder pattern shown in Fig. 1 will, in reality, be six lines.

The resultant powder pattern will be quite congested but with the above knowledge, sense can easily be made out of it. Figure 2 shows the resultant ESR spectra, which is the derivative of the absorption spectra. The lines at $\pm 4D$ are not shown in the figure, but if one increases the signal-to-noise ratio by about 20, they can readily be seen. The two outer lines are just the two outer hyperfine lines from the $\pm 2D$ lines. The next hyperfine lines from the $\pm 2D$ lines can also be seen, i.e., the fourth lines from the ends. The third and fifth lines from the ends are the two outer hyperfine lines from the $\pm D$ lines. They are about four times larger than the $\pm 2D$ lines. The rest of the spectra is quite messy but one can actually account for most of the wiggles and lines when the second-order splitting of the $\pm \frac{1}{2}$ to $\mp \frac{1}{2}$ transitions is also taken into account.

Once the spectrum is understood, it merely remains to measure the intensity of the lines as a function of concentration. The intensities of the outer hyperfine lines of the $\pm 2D$ and $\pm D$ lines were used since they did not overlap with any other lines. The intensities were measured and compared with the intensity of a line from Cr^{3+} in a single crystal of GASH which was oriented so that the spectra would not interfere with the Mn^{2+} spectra.

RESULTS

Figure 3 shows the results of $\log(I/I_0)$ versus c , which should be a straight line with slope $-n$ since

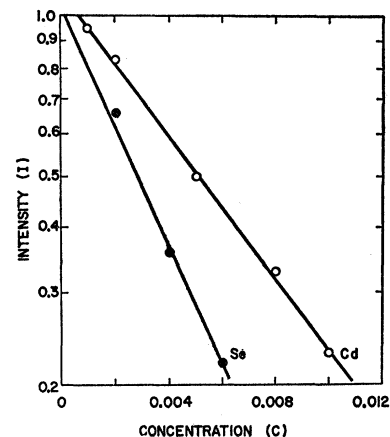
$$\log(I/I_0) = n \log(1-c) \approx -nc. \quad (3)$$

For the addition of Cd a value $n = 157$ is obtained. This

¹³ G. Burns, J. Appl. Phys. **32**, 2048 (1961).

¹⁴ B. T. Feld and W. E. Lamb, Phys. Rev. **67**, 15 (1945).

FIG. 3. Intensity versus concentration for Mn^{2+} in the system $(\text{Zn}_{1-c} + \text{Cd}_c)\text{S}$ and $\text{Zn}(\text{S}_{1-c} + \text{Se}_c)$.



corresponds to the Cd being on any of the Zn sites within a critical sphere of radius 11.5 Å. For the addition of Se, $n = 270$ is obtained. This corresponds to a critical sphere of radius 13.8 Å.

Actually, as can be seen in the figure, $I \neq I_0$ for $c = 0$. The reason for this is not known. It is conceivable that the addition of Cd or Se forces a small fraction of the manganese that might be presented in the $3+$ or $4+$ state into the $2+$ state. Or perhaps a small amount of Mn^{2+} is expelled during the reaction if no Cd or Se is present.

To calculate theoretically the wipe-out number, one must know the bandwidth of the experiment. Actually, no matter how close the Cd gets to the Mn, the ESR of the Mn^{2+} must appear somewhere. The point is that, in this experiment, one only looks at the positions of the undisplaced ESR line. The lines in Fig. 2 are about 15 G wide. This is a bit larger than the values found in single crystals¹² and is undoubtedly due to the fact that one is observing the derivative of the powder pattern rather than of a single crystal spectra. Thus, the wipe-out numbers refer to a change of D by more than 15 G.

The size of the critical sphere found in these ESR experiments is of the same order as that found in many of the alkali halide, etc., experiments.^{6,8,9} This at first sight was surprising since the D term should be determined mostly by overlap with the nearest neighbors of the Mn^{2+} . What is possibly happening is that the impurities produce dipole moments due to difference in size from the lost lattice as in the alkali halides.⁶⁻⁸ These dipoles can distort the charge distribution in the neighborhood of the Mn^{2+} ion. Thus, one can obtain large wipe-out numbers.

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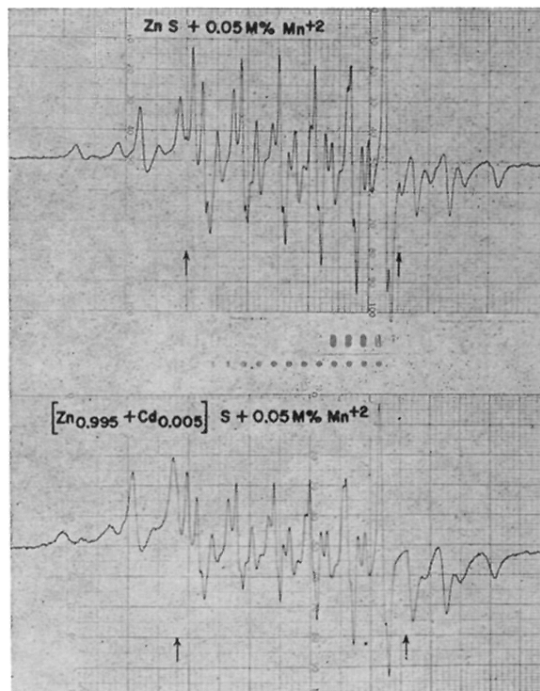


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