

EPR Concentration Dependence in Magnetically Diluted Crystals with Strong Spin–Spin Interaction

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Experimental investigations of electron paramagnetic resonance have been made in ionic crystals using diamagnetic samples with paramagnetic impurities and also in solid solutions in a large range of concentration. There exist cases in which neither the moment nor the statistical method could until now give even a qualitative explanation of the EPR linewidth and amplitude concentration dependence experimentally observed. In particular, this is true for the MnO–MgO solid solutions observed in the concentration range 10^{-3} to 0.8. It is believed that it is necessary to take into account spin–spin interactions (although not very small interactions) and magnetic clusters. A numerical statistical method, making no use of perturbation theory with respect to the interaction, is presented for considering multiparticle spin–spin interactions. A universal computer program using the ALGOL-60 language has been elaborated and applied, and the results for MnO–MgO solid-solution polycrystalline powders are given. Despite ambiguity concerning the literature data on the exchange constants and the small number of neighbors used ($n = 5$), the nonmonotonic character of the experimental curves giving the linewidth and amplitude concentration dependence may be qualitatively explained by the influence of the dipolar and exchange interactions.

I. INTRODUCTION

Many experimental investigations of electron paramagnetic resonance in ionic crystals have been made using diamagnetic samples with paramagnetic impurities; some solid solutions in a large range of concentration have also been investigated. To calculate the spin–spin broadening of the EPR line, the moment method was first used (I) under the following two suppositions. The constant applied magnetic field H_0 is strong enough to consider the spin–spin interaction as a small perturbation and the distribution of magnetic ions inside a sample is homogeneous. This approach leads to a linear growth of the EPR linewidth with increasing concentration c of magnetic ions; the lineshape is Lorentzian at low concentrations and becomes more and more Gaussian as the concentration increases.

These theoretical results are often not in agreement with experimental data (see, for example (2, 3)); hence new approaches have been proposed using statistical methods. In Ref. (3) a theory of this kind was presented that takes into account (in an exact manner) only two-particle interactions and neglects crystal structure details, both conditions implying low-concentration cases. The theory predicts the same lineshape as the

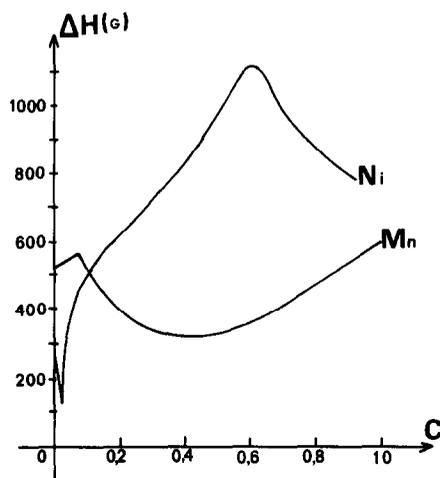


FIG. 1. Experimental diagram of the EPR absorption linewidth concentration dependence: MnO-MgO (4-6) and NiO-MgO (7) solid solutions.

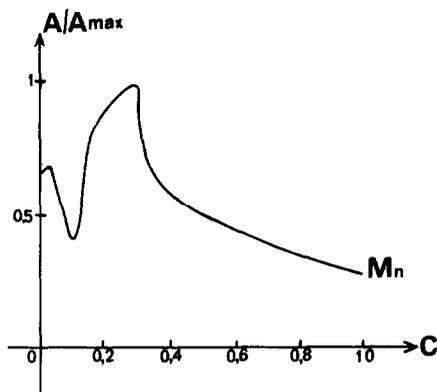


FIG. 2. Experimental diagram of the EPR absorption line amplitude concentration dependence: MnO-MgO solid solutions (4-6).

moment method, and a monotonic growth of linewidth with increasing concentration. In this way some experimental data have been interpreted successfully (3).

On the other hand, in many cases neither the moment nor the statistical method could until now give even a qualitative explanation of the experimentally observed EPR linewidth and amplitude concentration dependence. Two typical examples of this fact are MnO-MgO (4-6) and NiO-MgO (7) solid solutions. In both cases, the curves representing the dependence mentioned possess maxima and minima (see Figs. 1 and 2).

Two causes of this discrepancy may be pointed out for the systems considered at the concentrations in question. First, the spin-spin interactions are not very small. For example, in MnO-MgO solid solutions at $H_0 \simeq 10^3$ G, the dipolar interaction is of the same order of magnitude as the Zeeman interaction, and the nearest-neighbor exchange interaction is two orders higher. Second, magnetic clusters containing a substantial number of particles occur. Thus according to (8), in crystals possessing MnO symmetry at $c \simeq 0.1$, which means 1 Mn²⁺ for 9 Mg²⁺ ions, the sum of the formation probabilities for the nearest-neighbor clusters containing 1, 2, and 3 magnetic particles amounts only to about ± 0.5 .

In this paper, experimental results concerning MnO-MgO solid-solution polycrystalline powders (4-6) are compared with theoretical results obtained by means of a new statistical method (9). Solid solutions with a concentration range 10^{-3} to 0.8 were obtained by heating various MnO-MgO mixtures to 1000°C in a pure hydrogen stream. After a crystallographic and structural study aimed at verifying the preparation of the solid solutions, the authors measured the magnetic susceptibility as a function of temperature with a Foner magnetometer and calculated the exchange integrals between Mn²⁺ ions.

A three-wave interferometer (10) was used to study the EPR absorption and dispersion lines in these solid solutions at X-band frequency. The results obtained show an "irregular" concentration dependence of the lines. The lineshape for MnO is Lorentzian, and with decreasing concentration it becomes different but not Gaussian. An attempt was made to interpret the experimental lines, accepting the existence of a complex hyperfine structure due to the pairs and triplets of manganese ions.

Here a numerical statistical method (9) for considering multiparticle spin-spin interactions that makes no use of perturbation theory with respect to the interactions is presented (Sections II). Two model problems are treated by means of this method using computer techniques (Section III), and the results obtained are used to discuss the experimental data on the EPR concentration dependence (Section IV).

II. METHOD

Let us consider a magnetically diluted crystal (solid solution) containing N magnetic particles placed in an applied magnetic field $\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_1 \cos \omega t$, where $H_1 \ll H_0$, $\mathbf{H}_1 \perp \mathbf{H}_0$, and ω is large enough to treat the spin system as isolated from the lattice. In the absence of the rf field $\mathbf{H}_1 \cos \omega t$, the Hamiltonian (in frequency units) of the spin system may be written as

$$\mathcal{H}_0 = g\beta H_0 \sum_i S_z^{(i)} + \sum_{i,k} \sum_{\mu,\nu} U_{ik}^{\mu\nu} S_\mu^{(i)} S_\nu^{(k)}, \quad [1]$$

where the S are spin operators defined in the spin state space; i, k and μ, ν denote the magnetic particles and the coordinate axis indices, respectively; and the parameters $U_{ik}^{\mu\nu}(\mathbf{r}_i, \mathbf{r}_k)$ characterize spin-spin interactions. The position vectors \mathbf{r}_i and \mathbf{r}_k of the particles i and k are given by the expressions

$$\mathbf{r}_i = \sum_{j=1}^3 n_{ij} \mathbf{l}_j,$$

where the $\mathbf{l}_{1,2,3}$ are translation vectors of the magnetic lattice and the $n_{1,2,3}$ are positive integers with the greatest possible values $N_{1,2,3}$ corresponding to each concentration considered.

The conventional scheme of induced transitions can be applied to the spin system as a whole, giving the frequency dependence of the EPR absorption spectrum shape function

$$g(\omega) \equiv \sum_{a,b} |(a|\mathcal{H}_1|b)|^2 \delta[(E_a - E_b) - \hbar\omega], \quad [2]$$

with the sum taken over all the spin system stationary states a and b .

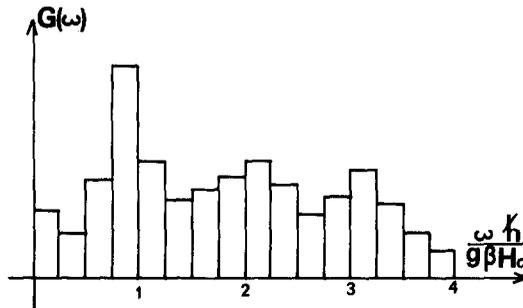


FIG. 3. Typical diagram of the calculated total absorption step function.

The solution of the eigenvalue problem $\mathcal{H}_0 \Psi_a = E_a \Psi_a$, that is, the set of E_a and Ψ_a (the parameters $U_{ik}^{\mu\nu}$ are specialized according to the kind of spin-spin interaction in question) gives the function $g(\omega)$. Consider the graph of this function. Let us divide the ω axis of the graph into a large number of small intervals of center frequency ω_l and width Δ , and let the step function $g(\omega)$ be defined whose value g_l for all the ω values in the range

$$\left(\omega_l - \frac{\Delta}{2}\right) < \omega < \left(\omega_l + \frac{\Delta}{2}\right)$$

equals the sum of the $g(\omega)$ values corresponding to the range considered. To obtain the absorption spectrum experimentally observed, a large number of functions $g(\omega)$ are calculated using sets of the ion positions chosen at random, and the results are averaged to give the new step function $G(\omega)$. The number of sets taken into account may be chosen according to conventional statistical procedure (see, for example (12)).

From the results of the numerical experiment described different kinds of information about the magnetic resonance absorption for an arbitrary (but certainly not very large) concentration may be obtained. A typical $G(\omega)$ diagram is shown in Fig. 3; one sees distinctly separate absorption lines of the spectrum. Having obtained such a diagram, one can attempt to approximate each line by some function of the form $\phi(\omega)$ minimizing the expression

$$\Phi \equiv \sum_j \left[\int_{\Delta_j} d\omega \phi(\omega) - G(\omega_j) \Delta_j \right]^2. \quad [3]$$

In particular, in the symmetrical line approximation one could try to use the mixed "Lorentz-Gauss" function

$$\phi(\omega) = \frac{A \exp[-B(\omega - \omega_0)^2]}{1 + D(\omega - \omega_0)^2}. \quad [4]$$

The only way to realize practically the statistical method outlined is to consider a "minisample" containing the magnetic ion number $n \ll N$ and to use a computer

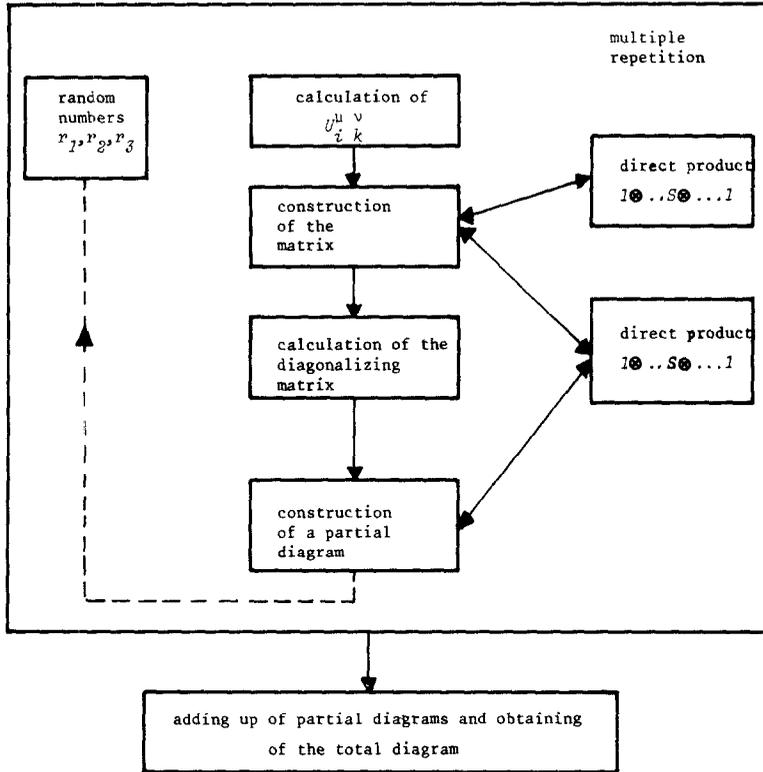


FIG. 4. General scheme of the computer program.

technique. A universal program for a computer using the ALGOL-60 language has been developed. The general scheme of the program is shown in Fig. 4. The following information has been introduced into the program: lattice type (that is, vectors $\mathbf{l}_{1,2,3}$); magnetic ion number n ; concentration c (that is, numbers $N_{1,2,3}$ corresponding to n instead of N ; Section II); spin S ; spin-spin interaction parameters; H_0 value and \mathbf{H}_0 and \mathbf{H}_1 orientation. To treat the eigenvalue problem in question (see Section II), the modified Jacobi method was used (see, for example (13)).

III. MODEL PROBLEMS

Two model problems were treated using the method described in Section II. In both problems the magnetic lattice symmetry is that of Mn in MnO, with a nearest-neighbor distance of 3 Å; $n = 5$, which makes it possible to consider concentrations up to $c =$

0.2; $S = \frac{1}{2}$; the dipolar interaction is taken into account for all five magnetic ions. The difference between the problems concerns the kind of exchange interaction considered. In the first problem it is $U_{ik}^{\mu\nu} = E_0 \exp(-\alpha r_{ik}) \delta_{\mu\nu}$ with $E_0/g\beta H_0 = 4 \times 10^3$ and $\alpha = 1 \text{ \AA}^{-1}$, which gives in the case considered, $H_0 = 8 \times 10^2 \text{ G}$, (see Section III) the exchange constant value $E^{nn} \simeq 85 \text{ K}$ for the first nearest neighbors and $E^{nnn} \simeq 26 \text{ K}$ for the next

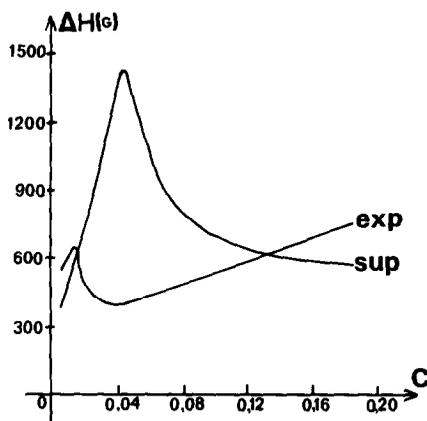


FIG. 5. Calculated diagram of the EPR absorption linewidth concentration dependence for the two model problems considered in Section III.

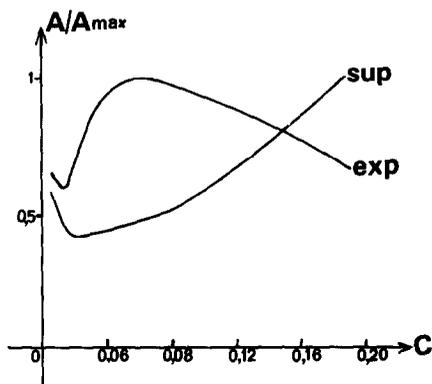


FIG. 6. Calculated diagram of the EPR absorption line amplitude concentration dependence for the two model problems considered in Section III.

ones. In the second problem no general formula for the exchange interaction is supposed, and the "superexchange" case $E^{nn} < E^{nnn}$ is considered, namely, $E^{nn} = 8.9 \text{ K}$ and $E^{nnn} = 10.6 \text{ K}$ (these are the data given in (14) for MnO); E^{nn} and E^{nnn} are the only exchange constants considered.

First, a single-crystal case was considered for a fixed (but arbitrary) orientation of H_0 with respect to the crystal axes and $H_0 = 8 \times 10^2 \text{ G}$. For each concentration value 50 random number sets were taken into account. The corresponding central linewidth and amplitude concentration dependence are shown in Figs. 5 and 6.

Second, a calculation was made for a powder sample, but only in the superexchange case with the same E^{nn} and E^{nnn} values and $H_0 = 33 \times 10^2$ G. To perform the direction averaging, one needs much larger random number sets in the powder case than in the single-crystal case. The calculation was considerably simplified by means of the conventional secularization of the dipolar interaction (see (15)), but still it was necessary to take into account 180 sets for each concentration value. As a result, the central linewidth concentration dependence curve was found to be similar to that shown in Fig. 5 for the superexchange case. The curve possesses a maximum at $c \simeq 0.02$, but the linewidth values are unexpectedly large: from 2×10^3 to 4×10^3 G. A possible cause of this strange "broadening" may be the secularization mentioned; to check this explanation, it would be necessary to perform the calculation taking into account the total (not secularized) dipolar interaction.

IV. DISCUSSION OF SOME EXPERIMENTAL DATA

Although a very small n (Section II) was used ($n = 5$; see Section III), a comparison between Figs. 1 and 2 and Figs. 5 and 6 shows that the nonmonotonic character of the experimental curves giving the linewidth and amplitude concentration dependence may actually be qualitatively explained by the common influence of the dipolar and exchange interactions, as has been suggested in (4-6), and that this explanation may apply to both kinds of exchange interaction considered in Section III.

As to a quantitative explanation of the experimental data in question, the following circumstances are to be taken into account (we confine ourselves to the data reported in (4-6)).

First, the calculation described in Section III was made for $S = \frac{1}{2}$, whereas Mn^{2+} ions possess $S = \frac{5}{2}$. However, this circumstance does not seem to be serious. The point is that the influence of the spin value on the absorption lineshape strongly depends on the crystalline field, which is small in MnO-MgO solid solutions (see, for example (15)).

Second, there is a large ambiguity concerning the literature data on the exchange constants E^{nn} and E^{nnn} in general and, for the substance discussed, in particular. Here are some examples: in (4-6) the values $E^{nn} = 11$ K, $E^{nnn} = 13$ K were reported on the basis of the results of the static magnetic susceptibility measurements performed on paramagnetic MnO ; in (14) the values $E^{nn} = 8.9$ K, $E^{nnn} = 10.6$ K were given with reference to the spin-wave investigations in antiferromagnetic MnO ; in (16) one finds the values $E^{nn} = 28$ K, $E^{nnn} = 1.4$ K obtained from the exchange-coupled-pair EPR study for the Mn ion concentration value of approximately 0.01. This second circumstance makes it very difficult to carry out the quantitative explanation mentioned above, because the exchange constant values are very important in the framework of the calculation scheme described in Section II.

It appears possible to use the method developed in Section II to obtain the exchange constant values experimentally if the exchange interaction is strong enough. In fact, given experimental data on the EPR concentration dependence for some types of magnetic ions (see Section I), one can try to perform a set of numerical experiments (see Section II) with different exchange constant values in the hope of determining values ensuring satisfactory agreement of the corresponding numerical experiment results with the experimental data mentioned.

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