PHYSICAL REVIEW B VOLUME 50, NUMBER 5 1 AUGUST 1994-I

Electron-paramagnetic-resonance spectra of Ni^{2+}-doped $Zn(BF_4)_2 \cdot 6H_2O$: Temperature and concentration dependence

W. Sano
Instituto de Física, Universidade de São Paulo, Caixa Postal 20516, 01452-990 São Paulo, São Paulo, Brazil

J. B. Domiciano
Departamento de Física, Universidade Estadual de Londrina, Caixa Postal 6001, 86051-970 Londrina, Paraná, Brazil

J. A. Ochi
Instituto de Física, Universidade de São Paulo, Caixa Postal 20516, 01452-990 São Paulo, São Paulo, Brazil

(Received 4 October 1993; revised manuscript received 28 March 1994)

The single-ion spin Hamiltonian parameters have been determined for zinc fluoroborate hexahydrate doped with Ni^{2+} ($3d^8$, $S=1$) and compared with those obtained for nickel fluoroborate hexahydrate. To account for the differences observed, EPR for several concentrations ($x=0.005$ to 1) was studied from room to liquid-helium temperature. Between 4.2 and 1.5 K, for low doping, they are constant with $g_{\parallel}=2.229\pm0.006$, $g_{\perp}=2.261\pm0.025$, and $D=-(0.1291\pm0.0008)\ \mathrm{cm}^{-1}$. Appropriate values for nickel fluoroborate are nearly the same but they are weakly temperature dependent, attributed to a ferromagnetic interaction. At higher temperatures these parameters are remarkably concentration dependent. Two main lines arise in parallel orientation. For concentrations up to $x\approx0.04$ and at 77 K, they show asymmetrically distributed satellite lines outside the more intense central portion. The satellite lines seem to increase with concentration but only those assigned to a ferromagnetic-coupled first-neighbor pair survive the simultaneous broadening effect. As the broadening is asymmetric, the lines' centers shift smoothly outwards. At $x\approx0.7$, we observe maximum broadening; for larger x no structural detail is seen and the spectra are progressively exchange narrowed. At the same time, the two lines are drawn together. The linewidth dependence on concentration indicates that the Ni ions have randomly occupied the Zn sites as expected, and that the contribution from spin-lattice relaxation practically does not change with concentration. We conclude that the differences in the spin Hamiltonian parameters are due essentially to magnetic interactions throughout the whole temperature range.

I. INTRODUCTION

Electron paramagnetic resonance (EPR) is a very sensitive technique available currently to study Ni^{2+} centers for a large number of phenomena like phase transitions,[1] magnetic interactions,[2] etc. In our previous works, we reported EPR of $Ni(BF_4)_2 \cdot 6H_2O$, nickel fluoroborate hexahydrate, hereafter referred to as NFB, and Ni^{2+}- and Mn^{2+}-doped isomorphous zinc fluoroborate hexahydrate (ZFB), $Zn(BF_4)_2 \cdot 6H_2O$. The temperature dependence (100–300 K) of the spin Hamiltonian parameters,[3–5] linewidths[3,4] and angular variations[3,5,6] of the spectra were reported. An apparent phase transition was detected in ZFB but not in NFB, characterized by anomalies in zero-field splitting (Refs. 4,5) and g factors.[4]

In the present work we have extended the EPR study of Ni^{2+}-doped ZFB, changing the molar concentration of Ni from $x=0.005$ to 1 to investigate the magnetic-interaction effect on the spectra. We will show that this type of interaction is responsible for differences in the spin Hamiltonian parameters between diluted and pure NFB crystals and for anomalies that we have reported as a phase transition. These features were clarified with measurements down to liquid-helium temperatures.

II. CRYSTAL STRUCTURE, SAMPLE PREPARATION, AND EQUIPMENT

ZFB forms a pseudohexagonal[7] lattice equivalent to a body-centered orthorhombic structure with lattice constants $a=7.62$, $b=13.20$, and $c=5.30$ Å. For the isomorphous[7] NFB they are respectively 7.66, 13.27, and 5.16 Å. The $(Ni \cdot 6H_2O)^{2+}$ octahedron site is at the center of another flattened octahedron formed by BF_4 molecules. Their trigonal axis is common, pointing along the c axis. It is easily identified as the needle growth axis in our monocrystals.

Samples were prepared using all reagents with paramagnetic-impurity content below 1 ppm. As the commercially available fluoroboric acid was not so pure we prepared it by reacting high-purity HF and H_3BO_3. The resulting HBF_4 was reacted with ZnO and $NiCO_3$. Each solution was mixed in the desired proportions. It was maintained in a water bath at 37.0 °C allowing slow evaporation for some days until crystals shaped like triangular-based prisms of about 2 mm long were grown. The true molar concentration of Ni atoms in the crystals was measured by optical absorption[8] of the solutions obtained by dissolving weighed crystals in known volumes

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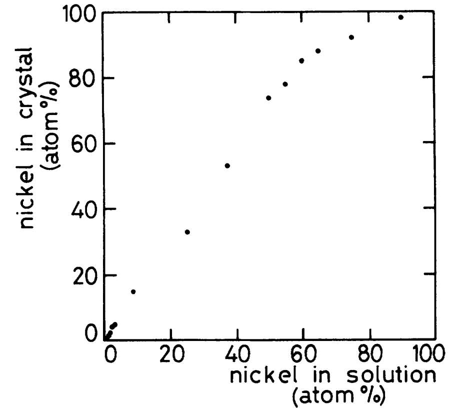

FIG. 1. True concentration of Ni^{2+} doped in $Zn(BF_4)_2 \cdot 6H_2O$ monocrystals with the mother solution molar percent concentration.

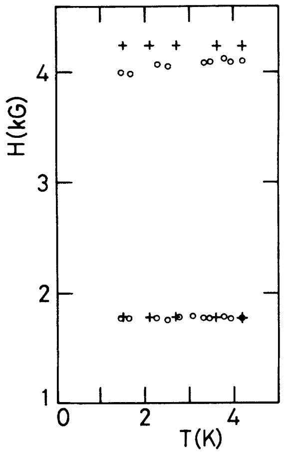

FIG. 2. Temperature dependence of the center of the EPR lines at liquid-helium temperatures for samples with molar concentration of Ni $x = 0.027$ (crosses) and $x = 1$ (open circles).

of distilled water. The Ni content was always higher in the crystal than in the mother solution, as is illustrated in Fig. 1. The green color of the samples was more intense for higher concentrations. Powder x-ray diffraction confirmed the expected structure.

EPR spectra were obtained in a conventional X-band, homodyne, JEOL model JES-PE-3X spectrometer. Temperature was varied using JEOL accessories with nitrogen-gas flux from 100 to 300 K. At 77 K an insertion-type Dewar vessel was used. Below 77 K a superheterodyne homemade spectrometer with sealed cavity immersed in liquid nitrogen or helium was used. Lower-temperature measurements were done by pumping on the liquid bath.

III. LOW-TEMPERATURE SPECTRA (4.2–1.5 K)

The spin Hamiltonian ascribed to Ni^{2+} ($3d^8, S = 1$) is

$$H = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + D S_z^2 ,$$

where $g_{\parallel}$ and $g_{\perp}$ are the g factors with the external magnetic field applied parallel and perpendicular to the distortion axis. The detailed procedure to obtain these parameters was described elsewhere.[3] Angular variation of the spectra indicate that the trigonal distortion is preserved along the c axis down to liquid-helium temperatures.

In Fig. 2 we show the thermal variation of the center of the lines with the magnetic field applied parallel to the trigonal axis. Results for one diluted sample and for NFB are shown for comparison. For the diluted crystal both lines are constant with temperature. The low-field line centers coincide for both samples within the experimental error. The difference is observed in the high-field lines, where the NFB lines are slightly lower and fall off slowly on lowering the temperature. In consequence, this behavior produces higher values for $g_{\parallel}$ and lower values for D. This is so because for $D < h\nu$ (valid for $T < 125$ K for our samples), $g_{\parallel}$ and D are given[9] by

$$g_{\parallel} = 2h\nu[\beta(H_{z1} + H_{z2})]^{-1} ,$$

$$D = h\nu(H_{z2} - H_{z1})(H_{z2} + H_{z1})^{-1} ,$$

where H_{z1} and H_{z2} are the low- and high-field centers of the lines, respectively. In the diluted sample, the constant $g_{\parallel}$ and D parameters indicate that no deformation or appreciable lattice vibration is present. Thus the variation in NFB can be attributed to the spin-spin interaction. Dipolar interaction in noncubic lattices and ferromagnetic exchange interaction shift the center of the lines[10] as we observed. However, considering that the temperature was not sufficiently low nor the microwave frequency sufficiently high to measure first-moment shifts accurately, this conclusion is mainly qualitative.

The relative intensity of the EPR lines is affected by population differences in the spin energy levels at liquid-helium temperatures. The low-field line intensity for the diluted sample remained practically unchanged with temperature while for the high-field line it was 34% higher at 4.2 K compared to that at 1.5 K. This is an indication that the spin doublet is lower than the singlet ($D < 0$) in our crystals.

IV. CONCENTRATION-DEPENDENT SPIN HAMILTONIAN PARAMETERS g AND D

In Table I we give representative parameter values for diluted samples. They are the best values for single-ion

TABLE I. Temperature dependence of the single-ion spin Hamiltonian parameters obtained from the sample with molar concentration $x = 0.015$, except for 4.2–1.5 K where the $x = 0.027$ sample was used.

T (K)	$g_{\parallel}$	$g_{\perp}$	D (cm^{-1})
300	2.240±0.012	2.250±0.012	−0.620±0.004
100	2.270±0.014	2.287±0.016	−0.2314±0.0020
77	2.270±0.006	2.263±0.028	−0.1898±0.0009
55	2.218±0.006	2.284±0.028	−0.1612±0.0009
4.2–1.5	2.229±0.006	2.261±0.025	−0.1291±0.0008

spin Hamiltonian parameters as we have taken advantage of the dilution effect that minimizes the linewidth. At 77 K and below, the main lines have an intense and nearly symmetric central portion with the width so small that some satellite lines appear. The existence of these lines suggests that the spectra have a complex structure. Increasing concentration seems to alter the intensity and the number of components producing asymmetrically broadened spectra. For NFB the spectra are more symmetric, exchange narrowed, and no structural detail can be observed even at liquid-helium temperatures.

In Table II we present similar parameters for NFB. The small departures from those at liquid-helium temperatures shown in Table I are due to spin-spin interaction as described in Sec. III. At high temperatures D is about 10% smaller than the values fitted for diluted samples. As the variation in g factors with concentration is not so meaningful we will not analyze it. In Fig. 3 we depict the thermal variation of D for some representative concentrations. The low-temperature side of this figure shows that D stops decreasing and seems to converge to a same value. It is on the high-temperature side that a remarkable difference with concentration is seen. To understand it let us show the concentration-dependent spectra at 77 K in Fig. 4. For $x=0.015$ the linewidth is considerably reduced and satellite lines are disclosed. Placed at an intermediary position between the two main lines and nearer the low-field line, the most intense and narrow of the subsidiary lines is due to a $\Delta m=2$ transition also known as the "forbidden" line.[11] For a more concentrated sample two satellite lines sited at the inner position (one at the right side of H_{z1} and the other at the left side of H_{z2}) are particularly remarkable in their intensity and constancy (see Fig. 4 for $x=0.15$). They alter their sides of the spectra considerably and persist up to $x \approx 0.7$. The spectra are simultaneously broadened with increasing concentration, suggesting that more lines have been generated such that the structural detail is gradually disappearing. As these components are indeed asymmetrically distributed, the "centers of gravity" of these groups smoothly shift out, which surely provides changes in the g and D values. The above-described intense satellite lines are probably related to ferromagnetic coupling between first neighbors, similar to that considered by Galkin, Kozhukhar', and Tsintsadze[12] in Ni:ZnSiF$_6$·6H$_2$O. This type of pair gives satellite lines more distant from the main line at the inside position, as in our spectrum of Fig. 4 ($x=0.15$). Pairs coupled antiferromagnetically should give similar lines at outside positions. At $x \approx 0.7$ when maximum broadening has taken place, the linewidth becomes progressively narrowed. In this way we concluded that each group of the complex structure of lines has been merged by exchange interaction.[13] Besides the exchange merging and subsequent narrowing of each main H_{z1} and H_{z2} group a drawing together also occurs (see the spectrum for $x=1$ in Fig. 4). This can be assigned to the exchange tending now to merge these groups as a result of its strengthening with concentration. This also changes the parameter values for NFB.

In our earlier work we have reported that there are two linear regions in the D versus T curve for diluted samples[4] with different slopes above and below 190 K. We have interpreted this as an anomaly due to a phase transition connected to the dynamic behavior of H$_2$O or BF$_4$ groups. A similar feature was not observed in NFB.[3]

TABLE II. Temperature dependence of the spin Hamiltonian parameters for NFB ($x=1$ sample).

T (K)	$g_\parallel$	$g_\perp$	D (cm^{-1})
300	2.311±0.025	2.226±0.025	−0.537±0.004
100	2.275±0.005	2.315±0.005	−0.1928±0.0010
77	2.254±0.020	2.366±0.020	−0.1703±0.0010
55	2.269±0.020	2.312±0.025	−0.1501±0.0010
4.2	2.27±0.04		−0.124±0.005

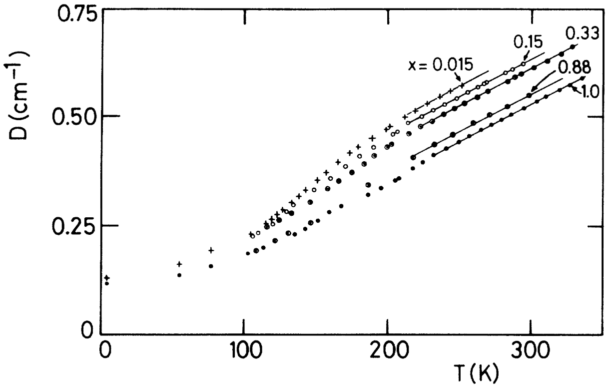

FIG. 3. Temperature dependence of the crystal-field distortion parameter for some molar concentrations x of Ni.

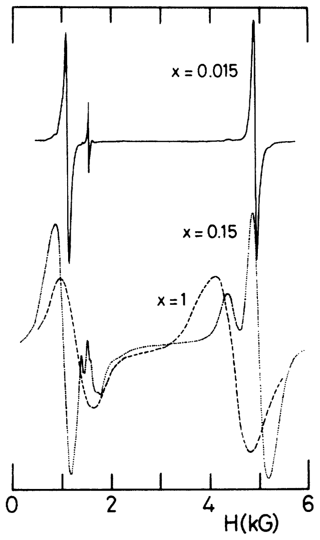

FIG. 4. EPR spectra with the magnetic field applied parallel to the crystal-field distortion for different molar concentrations x ($h\nu=0.3096$ cm^{-1}, $T=77$ K).

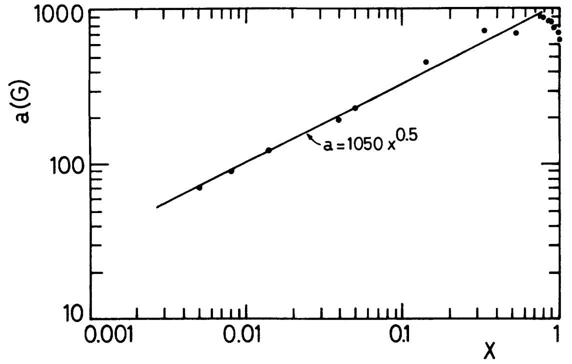

FIG. 5. Concentration dependence of the temperature-independent linewidth parameter.

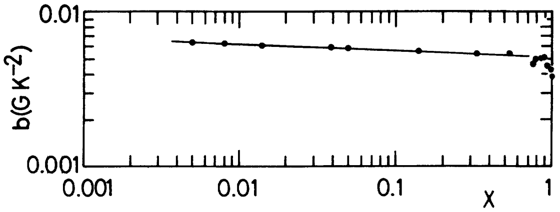

FIG. 6. Concentration dependence of the T^2 coefficient linewidth parameter. The straight line corresponds to $b=51x^{0.14}$ (10^{-4} G K^{-2}).

With the present measurements we can say that the above conclusion was drawn in the absence of low-temperature data. Actually, D changes in concavity at low temperatures for any concentration and goes to a constant value at liquid-helium temperature (shown in Fig. 3). This concavity change could still indicate a phase transition. The linear variation of the D versus T curve at high temperatures and the constant D value at low temperatures agree with the Walsh[14] model based on lattice vibrations. At intermediate temperatures the underlying physics is very difficult to determine. Therefore EPR alone cannot draw a sure conclusion about the existence of this phase transition.

V. MAGNETIC INTERACTION EFFECT ON LINEWIDTH AND FORM

In our previous works[3,4] we reported that the variation in linewidth at maximum slope is given by

$$\Delta H_{\mathrm{MS}} = a + bT^2 ,$$

where a represents the contribution from spin-spin interaction and the quadratic term is characteristic of the two-phonon Raman process of spin-lattice relaxation.[11] This law was verified in all the samples above 220 K. The a parameter varies as $x^{1/2}$ with concentration (shown in Fig. 5). This indicates that in the Ni-doping process the Zn lattice sites are populated with equal probability.[11] Above $x \approx 0.7$ the linewidth starts to decrease because of exchange narrowing.

The concentration dependence of the b parameter is shown in Fig. 6. It decreases very slowly, indicating that there is no appreciable change in lattice vibrations with concentration. At higher concentrations it is also affected by the exchange narrowing. Using a similar procedure to that of Rubins, Clark, and Jani[15] and taking the same values adopted by them for Δ and v for $NiSiF_6 \cdot 6H_2O$, we estimated the Debye temperature of ZFB ($x=0.05$) as $\Theta_D \approx 98$ K. That is of the same order as their $\Theta_D \approx 107$ K.

We have obtained nearly symmetric lines only below $x=0.05$ and above $x=0.7$. At intermediate concentrations we have analyzed only the outer half of the lines where no splittings were evident. Below $x=0.15$ the line was nearly Lorentzian and above it was nearly Gaussian. This is in fair agreement with the Kittel and Abrahams[16] theoretical prediction. These considerations are valid only at 77 K and below. At higher temperatures all the lines are considerably lifetime broadened in consequence of the spin-lattice relaxation effect, so that no structural vestiges remain and they are more nearly Lorentzian.

VI. CONCLUSIONS

Ni^{2+} dilution in zinc fluoroborate hexahydrate crystals was useful to narrow the EPR spectra to determine accurate single-ion spin Hamiltonian parameters. Differences in these parameters between diluted and pure nickel fluoroborate samples at first sight might be attributed to a little difference in the size of the lattice. However, the present work shows that spin-spin interactions do not merely broaden the spectra but also shift their centers even at high temperatures. Analyzing the concentration-dependent spectra, we concluded that magnetic interactions are the chief cause of these differences.

ACKNOWLEDGMENTS

W.S. wishes to thank Professor H. Ohkura for his encouragement and the use of his equipment and Dr. M. Matsuoka for his help, during his visit to Osaka City University (Japan), where experimental data below 77 K were obtained. This work was supported in part by Fundação de Amparo à Pesquisa do Estado de São Paulo, Conselho Nacional de Desenvolvimento Científico e Tecnológico, Coordenação de Aperfeiçoamento de Pessoal do Ensino Superior, and Financiadora de Estudos e Projetos.

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