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Ni^{2+} ions in $RbCdF_3$: An EPR study in the cubic and tetragonal phases

P. J. Alonso and R. Alcalá

Instituto de Ciencias de Materiales de Aragón (Universidad de Zaragoza—Consejo Superior de Investigaciones Científicas), Plaza San Francisco s/n, E-50009 Zaragoza, Spain

J. M. Spaeth

University of Paderborn, Fachbereich 6–Physik, Warburger Strasse 100A, D-4790 Paderborn, Federal Republic of Germany

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The EPR spectra of Ni^{2+} ions in $RbCdF_3$ occupying a Cd^{2+} substitutional site have been studied both in the cubic ($T > 124$ K) and in the tetragonal ($T < 124$ K) phase. In the cubic phase they are characterized by an isotropic g factor ($g = 2.34 \pm 0.01$). In the tetragonal phase the EPR spectra of Ni^{2+} are described by an axial spin Hamiltonian with $S = 1$. The g tensor does not change with temperature. The principal values are $g_{\parallel} = 2.321 \pm 0.005$ and $g_{\perp} = 2.295 \pm 0.005$. The crystal-field parameter D has a value of 12.23 ± 0.03 GHz at 77 K and decreases as the temperature increases. Below the transition temperature (124 K) it varies according to $D(T) = D_0|T - T_0|^{2\beta}$ with $D_0 = 1.75$ GHz, $T_0 = 124$ K, and $\beta = 0.25$. This β value compares well with those obtained by other techniques.

I. INTRODUCTION

$RbCdF_3$ has a cubic perovskite structure at room temperature (RT) and undergoes a structural phase transition at 124 K. This transition is of second order and consists of alternate tiltings of the fluorine octahedra around a $\langle 100 \rangle$ axis together with an elongation along the rotation axis.[1-4] Among other techniques, electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) spectroscopies of impurity transition-metal ions have been used to study this phase transition. Some of these studies correspond to Mn^{2+} and Fe^{3+} ions.[1-4] The electronic configuration of these ions is $3d^5$, which corresponds to a half-filled shell with a ^6S ground state the interaction of which with the lattice is expected to be small.

EPR studies of Ni^{2+} impurities in octahedral environments have been reported in different materials.[5-10] Because of its even number of electrons, Ni^{2+} is a non-Kramers ion and its EPR spectra are very sensitive to the interactions with the environment. Because of this it could give more detailed information about the phase transition in $RbCdF_3$ than the S ions. However, if strains are present in the crystal, broad EPR lines due to strain-spin coupling effects are usually observed, even in systems such as MgO and CaO (Refs. 8-10) where other transition ions show very narrow resonance lines. Although this broadening provides information about the strain field, it can be deleterious in studying phase transitions.

In this paper we present an EPR study of Ni^{2+} impurities doped into $RbCdF_3$. Both the cubic phase and the tetragonal one have been studied. In all the cases the spectra can be described with a spin $S = 1$, and in the low-temperature phase a tetragonal crystal-field term has to be included, which decreases as the temperature increases. A measure of the temperature dependence of this crystal-field contribution gives information about the critical exponent of the phase transition. On the other hand, the shape of the EPR lines is explained taking into account the residual strains in the crystal that have strong coupling with the Ni^{2+} spin. The lack of resolved superhyperfine (SHF) structure due to the strain-induced broadening makes it impossible to get any information about the rotation angle of the fluorine octahedra.

II. EXPERIMENTAL PROCEDURE

Single crystals of $RbCdF_3$:Ni were grown by the Bridgman technique using an rf heated furnace and vitreous carbon crucibles. The starting materials were RbF and CdF_2 with 0.5 mol % NiF_2.

EPR spectra were measured with a Varian E-112 spectrometer (X band). Measurements at liquid-nitrogen temperature (LNT) were taken using a quartz immersion dewar. For measurements at different temperatures a continuous flow helium cryostat (ESR-900) from Oxford Instruments or the variable temperature accessory (E-257) from Varian were used. The temperatures were measured with a copper-constantan thermocouple in contact with the sample. The estimated error was about ±0.5 K. The magnetic field was measured with an NMR gaussmeter Brucker NM305. The diphenylpicrylhydrazyl (DPPH) signal ($g = 2.0037 \pm 0.0002$) was used to determine the microwave frequency.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The EPR spectra of $RbCdF_3$:Ni crystals have been measured at different temperatures between 60 K and room temperature (RT). Above the transition temperature, T_c ($T_c = 124$ K, see Ref. 1) the spectrum is isotropic. It is shown in Fig. 1(a). This spectrum, which is as-

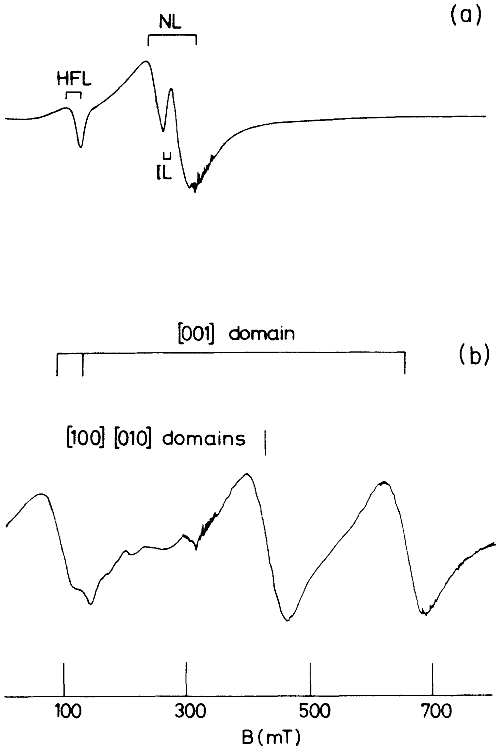

FIG. 1. EPR spectra of Ni^{2+} ions in $RbCdF_3$. (a) measured at about 140 K (cubic phase) and (b) measured at 77 K (tetragonal phase) in a polydomain sample with the magnetic field along a pseudocubic [001] direction. The weak structured signal at about 320 mT is due to traces of Mn^{2+} impurities.

sociated with Ni^{2+} ions on a Cd^{2+} site, consists of three lines. The broadest one (peak-to-peak width of about 75 mT) is centered at $g \approx 2.34$. It is designated as normal line (NL). Superimposed to it another narrower line appears with its phase inverted. This is called the inverted line (IL). Both NL and IL are fairly symmetric. Besides, a third line, at roughly half-field is observed. This last one, labeled HFL (half-field line) is strongly assymmetric, being more extended towards its low-field side.

This spectrum can be understood in the following way. The degenerated free-ion ^3F ground state of Ni^{2+} splits as a consequence of the crystal field. In an octahedral environment the orbital singlet $^3A_{2g}$ results to be the lowest-energy level. Using the spin Hamiltonian

$$H = g\,\mu_B \bar{\mathbf{S}} \cdot \bar{\mathbf{B}} \tag{1}$$

with $S=1$ and an isotropic g factor, an isotropic line is obtained which corresponds to the $|0\rangle$-$|\pm1\rangle$ magnetic dipole transitions. Due to the moderately high spin-orbit coupling the isotropic g factor of octahedrally coordinated Ni^{2+} departs from the free-electron value, g_e. In the framework of ligand field theory, it is given by[11]

$$g = g_e - \frac{8\lambda}{\Delta} \tag{2}$$

where λ is the effective spin-orbit coupling constant and Δ is the energy difference between the ground state $^3A_{2g}$ and the first excited one $^3T_{2g}(^3F)$. Optical absorption measurements give a Δ value of 6600 cm^{-1}. The observed g value (2.34 ± 0.01) can be obtained from (2) using a λ value of 280 cm^{-1} which is 86% of the free-ion value. Usually similar reductions due to crystal-field effects have been observed.

On the other hand, residual strains in the lattice introduce some departures from cubic symmetry and a distribution of splittings between the $|0\rangle$ state and the $|1\rangle$ and $|-1\rangle$ levels is obtained. In this way a broadening of the line associated with the $|0\rangle$-$|\pm1\rangle$ allowed transitions results. Broad EPR lines due to these transitions of Ni^{2+} in different crystals with an octahedral environment have been reported.[5-10] In the case of Ni^{2+} in MgO Smith *et al.*[12] have proved that the shape of this signal can be modified by thermal treatments of the crystals. The broadening was attributed to a distribution of crystal strains. These authors have also studied the shape of the $g=2.34$ EPR line of Ni^{2+} in MgO. Besides the broad EPR signal they have found that, when the microwave power is low enough, another line at about the same field position but with its phase inverted is also observed.

The same type of inverted phase line in the $g \approx 2.34$ signal is observed in our EPR spectrum shown in Fig. 1(a). Then we can interpret our results following the ideas of Smith *et al.*[12] The NL corresponds to the inhomogeneously broadened $|0\rangle$-$|\pm1\rangle$ transitions, while the IL correspond also to these transitions but it is due to those Ni^{2+} ions in sites having minimum strains in such a way that the strain-induced shift of the resonance is smaller than the homogeneous width of the EPR line.[12]

Moreover, the wide peak-to-peak width of the NL in our samples suggests that the inhomogeneous broadening due to strains is large and it is necessary to consider nondiagonal terms in the strain-spin coupling.[12] This effect also has been considered by McMahon[13] in the case of the EPR spectrum of cubic Fe^{2+} substitutional in MgO (also $S_{ef}=1$). Then the strain spin coupling induces mixing between the Zeeman states, and the otherwise forbidden $|-1\rangle$-$|+1\rangle$ transition becomes partially allowed. Its transition probability is strongly dependent on the strain field which, at the same time determines the resonance magnetic field. Taking these effects into account it is possible to explain the line, which roughly appears at half the magnetic field of the NL, and its asymmetry, being extended towards the low-field side (see Ref. 13 for detailed calculations of this shape).

In conclusion we can understand all the features of the EPR spectrum of Ni^{2+} ions in the cubic phase of $RbCdF_3$ with an isotropic spin Hamiltonian with $S=1$, which only includes a Zeeman term with $g=2.34$, and taking into account a fairly strong strain-spin coupling.

We will analyze now the Ni^{2+} EPR spectra in the tetragonal phase. The sample used in our experiments is a polydomain one. There are three different orientations for the domains, each of them having its C_4 axis parallel to one of the $\langle 100 \rangle$ pseudocubic axes.

In Fig. 1(b) the EPR spectrum of a $RbCdF_3$:Ni sample measured with the magnetic field along a $\langle 100 \rangle$ pseudocubic direction is shown. Three strong broad lines (peak-to-peak width of about 65 mT) together with another smaller one at about 140 mT are seen. As shown in the figure, the central line is due to Ni^{2+} ions in domains with the tetragonal axis perpendicular to the applied magnetic field $\mathbf{B}_0$. The other three lines come from nickel ions in the domains with the axis parallel to B_0. The strong lines at about 100 and 650 mT correspond to the allowed $|\Delta M|=1$ transitions. The small line at about 140 mT is due to the forbidden $|\Delta M|=2$ transition, which becomes partially allowed due to random lattice strains (see the following). In the tetragonal phase the EPR spectrum depends on the magnetic-field orientation. In Fig. 2 the circles represent the positions of the lines measured at liquid-nitrogen temperature (LNT) as a function of the angle θ between the dc magnetic field $\bar{\mathbf{B}}$ and the [001] direction when the field rotates in the (100) plane. This pattern indicates that the EPR spectrum of Ni^{2+} in the tetragonal phase can be described by the following spin Hamiltonian:

$$H=\mu_B B(g_\perp \sin\Psi S_x + g_\parallel \cos\Psi S_z) + D[S_z^2-\tfrac{1}{3}S(S+1)] \quad (3)$$

with $S=1$ and the z direction along the tetragonal axis of the domains. Ψ is the angle that the magnetic field makes with the z direction.

The lines positions calculated by computer diagonalization of the spin Hamiltonian given by Eq. (3) have been fitted to the experimental ones. The best fitting has been obtained for the following values of the parameters:

$$g_\parallel = 2.321 \pm 0.005 ,$$

$$g_\perp = 2.295 \pm 0.005 ,$$

$$D = 12.23 \pm 0.03 \text{ GHz} .$$

We want to point out that in the tetragonal phase spectra all the lines are broad as in the cubic phase. However, the peak-to-peak width depends on the orientation of the magnetic field with respect to the tetragonal axis. The minimum width is obtained when Ψ is close 45° ($\Delta H \approx 30$ mT). This can be also interpreted as a consequence of the strain-spin coupling. In a first approximation this coupling could be described by introducing a distribution of values of the D parameter. The derivatives of the resonance magnetic-field values as a function of the crystal-field parameter D are also dependent on the magnetic-field orientation but this dependence can neither explain the changes observed in the line widths with θ nor the observation of the $|-1\rangle$-$|+1\rangle$ resonance line (the small line at 140 mT) when the magnetic field is along the tetragonal axis. This suggest that also in the low-temperature phase the strain-spin coupling is strong enough and its nondiagonal terms are not negligible.

When the temperature changes the positions of the lines shift. The EPR spectrum of Ni^{2+} ions taken with the magnetic field along a pseudocubic $\langle 100 \rangle$ direction has been measured at different temperatures in the tetragonal phase. The analysis indicates that the lines can be described with the same spin Hamiltonian of Eq. (3) and with the same values for the g-factor but the crystal-field parameter D decreases as the temperature increases. In Fig. 3 the crosses represent the values of the D parameter as a function of temperature. This temperature dependence has been fitted to the expression

$$D(T)=D_0|T-T_0|^{2\beta} \quad (4)$$

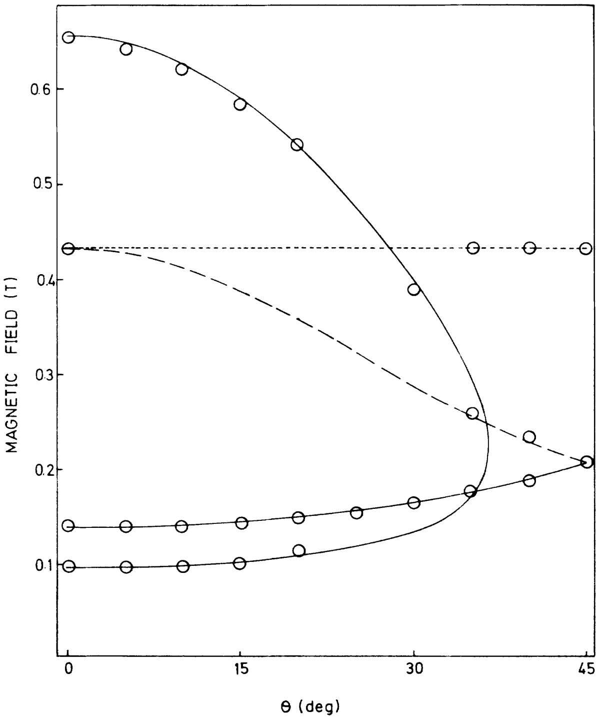

FIG. 2. Circles represent the positions of the observed EPR lines measured at 77 K in a polydomain sample as a function of the angle θ between the pseudocubic [001] direction and the static magnetic field when this rotates in the (100) plane. The lines represent the predicted evolution calculated using the spin Hamiltonian given by Eq. (3) with the values for the parameters given in the text. The different traces correspond to domains oriented in the three different directions.

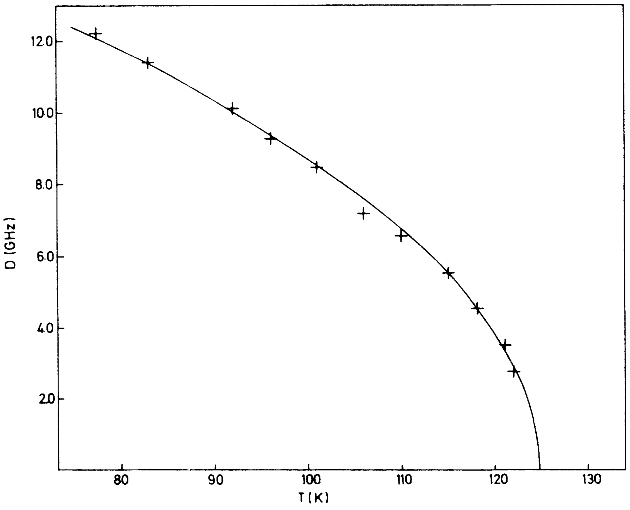

FIG. 3. The crosses give the values of the crystal-field parameter D for Ni^{2+} in the tetragonal phase. The continuous line corresponds to the predicted evolution given by Eq. (4).

and the best fitting is reached for the following values:

$$D_0 = 1.75 \pm 0.05 \text{ GHz} ,$$

$$T_0 = 124 \pm 1 \text{ K} ,$$

$$\beta = 0.25 \pm 0.02 ,$$

with a mean-square deviation of 0.17 GHz.

The dependence given by Eq. (4) can be understood considering that for small tilting angles ϕ of the fluorine octahedra with ϕ being the order parameter of the phase transition, the crystal-field coefficient D is a quadratic function of ϕ (Ref. 14) and taking into account the temperature dependence of the order parameter:[15]

$$\phi = \phi_0 |T - T_0|^{\beta} , \tag{5}$$

where β is the critical exponent of the phase transition.

The β value obtained from the data of Fig. 3 ($\beta \equiv 0.25$) is in good agreement with those obtained by Rousseau *et al.*[4] from EPR data of Fe^{3+} in RbCdF$_3$. It is also in agreement with the values for the critical exponent in the case of RbCaF$_3$ that has a similar phase transition. For this compound, slightly different β values have been obtained using different techniques: neutron-diffraction studies and Mossbauer experiments give $\beta = 0.25$,[16] single crystal x-ray diffraction[17] and NMR spectroscopy data[18] yield $\beta = 0.27$, while from EPR measurements[19] using a Kramers ion like Ni$^+$ a value of $\beta = 0.26$ is obtained.

Another source of information usually derived from EPR measurements is the tilting angle of the fluorine octahedra as a function of temperature. In the case of axial centers this information could be derived from the analysis of the SHF structure. However, due to the big broadening induced in our lines by strain-spin coupling no SHF structure could be resolved and consequently no information about the tilting angle can be given.

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