Electron Paramagnetic Resonance of Ni^{2+} in $BaZnF_4$ Single Crystals

S. Remme and G. Lehmann

Institut für Physikalische Chemie der Westfälischen Wilhelms-Universität Münster,
West Germany

K. Recker and F. Wallrafen

Mineralogisches Institut der Universität Bonn, West Germany

Z. Naturforsch. **41 a,** 619–622 (1986); received February 3, 1986

X-band EPR measurements of Ni-doped $BaZnF_4$ crystals revealed presence of three centers. Well-resolved hyperfine structure from ^{19}F nuclei at suitable orientations allowed assignment of the most intense spectrum to single ions on Ba sites. The occupation of Zn sites is considerably lower. The third spectrum is assigned to pairs of Ni^{2+} ions on adjacent Ba sites. Attempts to correlate the zero-field splitting (ZFS) patterns of the single ion spectra with the distortions of the first coordination spheres of Ba and Zn resp. with a single intrinsic ZFS parameter for both bridging and nonbridging ligands were equally unsuccessful as in the case of Mn^{2+}.

Introduction

EPR data for the d^8-ion Ni^{2+} in solids are still rather scarce, but numerous successful correlations of the zero-field splitting (ZFS) patterns for the d^5-ions Mn^{2+} and Fe^{3+} with the distortions of their first coordination spheres by application of the superposition model (SPM) [18] have stimulated analogous tests for non S-state ions also. Comparison of the available data for Ni^{2+} and Mn^{2+} in the same lattice sites in Table 1 shows the ZFSs to be on the average about two orders of magnitude larger for Ni^{2+}. If these ZFSs are also largely determined by the geometries of the ligands (this has been questioned for all non S-state ions for theoretical reasons [19]) much larger intrinsic ZFS parameters $\bar{b}_2$ (i.e. ZFSs per unit distortion) are required for Ni^{2+} than for Mn^{2+}. A rigorous test requires either investigation of a larger number of systems with axial site symmetries for the same ligands or more detailed investigation of systems with lower site symmetries for which the orientations of the principle axes are not completely fixed by symmetry. The dependence of the intrinsic ZFS parameters on bond distance also has to be determined in the same type of experiments. Judging from uniaxial stress measurements for Cr^{3+} [20] it may be completely different from that for Mn^{2+} and Fe^{3+} with a R^{-7} dependence. With this background in mind we investigated the system $BaZnF_4$:Ni with monoclinic (C_s) point symmetries for both Zn and Ba [21]. Corresponding data for Mn^{2+} are already available [22].

Table 1. Axial zero-field splitting parameters for Ni^{2+} and M^{2+} in the same lattice sites.

Host crystal	T/K	b_2^0/cm^{-1} (Ni)	b_2^0/cm^{-1} (Mn)	Ratio	Source
K_2ZnF_4	290	− 1.67	+ 0.0036	− 464	[1, 2]
K_2MgF_4	300	− 0.69	+ 0.0108	− 64	[3, 2]
$CsCdCl_3$	77	± 0.905	+ 0.0015	± 603	[4]
$CsMgCl_3$	293	± 1.918	+ 0.0305	± 63	[5]
	77	± 2.000	+ 0.0293	± 68	[5]
$CdCl_2$	77	± 1.35	+ 0.0015	± 900	[6]
$CsCdBr_3$	77	± 1.28	+ 0.0340	± 38	[7]
$CsMgBr_3$	77	± 1.70	+ 0.0930	± 18	[8]
$CdBr_2$	77	+ 0.220	− 0.0160	− 14	[9, 10]
LaMgNY*	77	− 2.164	− 0.02183	+ 99	[11, 12]
	4.2	− 2.217	− 0.02201	+ 101	[11, 12]
LaZnNY	77	− 2.212	− 0.02100	+ 105	[11, 12]
	4.2	− 2.265	− 0.2120	+ 107	[11, 12]
LaZn NX	77	+ 0.043	− 0.00626	− 7	[11, 12]
	4.2	+ 0.063	− 0.00703	− 9	[11, 12]
$ZnSiF_6 \cdot 6\,H_2O$	302	− 0.64	− 0.0130	+ 49	[13]
$MgSiF_6 \cdot 6\,H_2O$	77	± 2.16	+ 0.02623	± 82	[14]
$ZnTiF_6 \cdot 6\,H_2O$	298	± 1.38	− 0.01728	± 80	[15]
$Zn(BF_4)_2 \cdot 6\,H_2O$	308	± 0.631	+ 0.01003	± 63	[16, 17]

* Double nitrates of general formula $M(III)_2M'(II)_3(NO_3)_{12} \cdot 24\,H_2O$. *X* and *Y* denote different sites occupied by the transition metal impurities.

Reprint requests to Prof. Gerhard Lehmann, Institut für Physikalische Chemie, Schlossplatz 4, D-4400 Münster.

0340-4811 / 86 / 0400-0619 $ 01.30/0. – Please order a reprint rather than making your own copy.

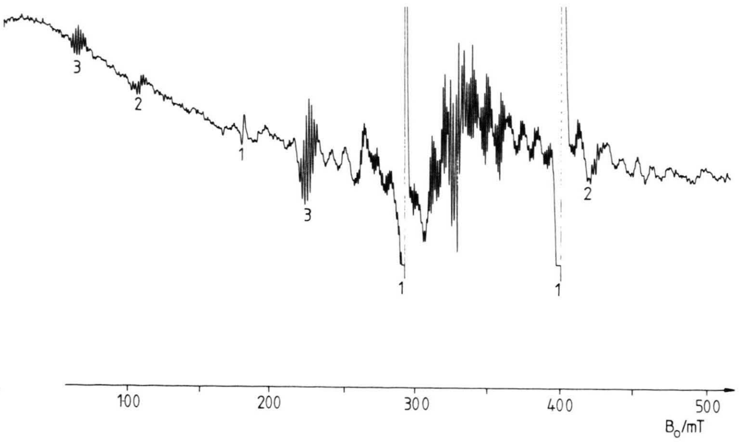

Fig. 1. EPR spectrum of Ni^{2+} in $BaZnF_4$ at 9.54 GHz and 293 K for $B_0 \parallel a$-axis. *1* Single ions on Ba sites, *2* single ions on Zn sites, *3* pairs on Ba sites.

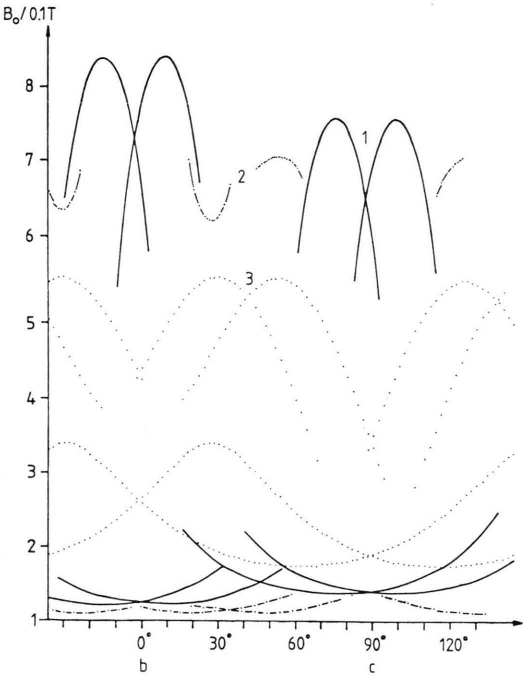

Fig. 2. Rotational diagram for Ni^{2+} in $BaZnF_4$ at 9.54 GHz and 293 K. The signals with extrema 12° from *b*- and *c*-axes (———) are the most intense ones, those with maxima near 0.34 and 0.55 T (·····) are of intermediate intensity.

Results and Discussion

A crystal with 0.55% Ni per Zn grown from the melt analogously to the Mn-doped ones [22] was investigated at X-band and room temperature. The spectra were rather complex as shown in the example in Fig. 1 and in the rotational diagram in Figure 2. They can be assigned to three different centers which are marked by different symbols. Well resolved hyperfine structures were observed for some transitions which aided in the assignment of the three spectra. In the spectrum of lowest intensity a septet hyperfine structure (Fig. 3) indicates a sixfold coordination by fluorine and thus occupation of Zn sites. The intensity ratios of the central transitions are considerably lower than calculated for six equivalent nuclei, but this can, at least qualitatively, be ascribed to the monoclinic site symmetry with five different bond distances. The spectrum of highest intensity with principal axes about 12° from the *b*- and *c*-axes must then be due to Ni^{2+} on Ba sites. No hyperfine structure could be detected in this spectrum, most likely as a result of the very irregular coordination by 11 fluorines with bond lengths ranging from 264 to 339 pm (compared to 196 to 211 pm for the Zn site). The at least nine hyperfine components present in the spectrum of medium intensity indicate presence of eight or more ligands. This center has the same orientations of principal axes as the Ni^{2+} on Zn sites with angles of about 30° to *b*- and *c*-axes. It can only be due to pairs of adjacent Ni^{2+} ions. Since the Ba sites are preferentially occupied, only pairs with at least one ion on a Ba site can be expected to occur in sufficiently high concentrations. The symmetry of the spectrum with the *a*-axis as one of the principal axes imposes further restrictions. The possibilities listed in Table 2 remain. While the first three combinations lie in the $b-c$ plane, the third one is aligned along the *a*-axes. The observed spectrum is seen to be best compatible with occupation of two adjacent Ba sites as also expected from the intensity ratio of the single ion spectra.

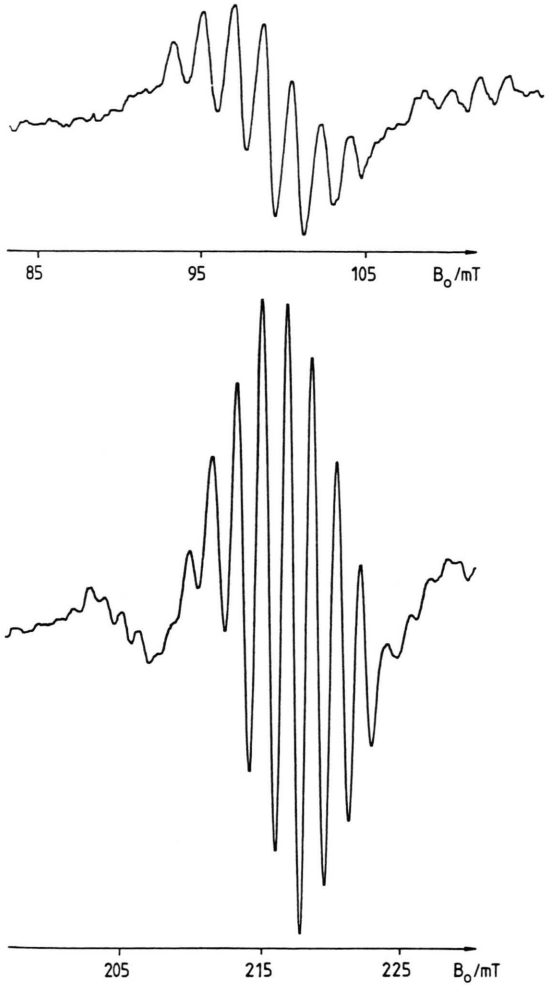

Fig. 3. ^{19}F hyperfine structure in two signals for $B_0 \parallel a$. a) Septet due to Ni^{2+} on Zn site with sixfold coordination, b) hyperfine structure with at least nine components, assigned to pairs of Ni^{2+} on adjacent Ba sites.

The spin-Hamiltonian parameters and direction cosines of their principle axes for the single ion spectra are listed in Table 3.

Table 2. Possbile combinations of sites for pair spectra.

Combination	Angles [degree to b and c]	Distance [pm]
Zn–Zn	49/41	388
Zn–Ba	72/18	354
Ba–Ba	34/56	515
Ba–Ba	90	421

Table 3. Spin-Hamiltonian parameters and direction cosines of principal axes for single ion spectra of Ni^{2+}.

	Ba site			Zn site		
g_{iso}	2.28(3)			2.28(3)		
b_2^0/cm^{-1}	0.655(6)			0.96(1)		
b_2^2/cm^{-1}	0.39(1)			0.17(1)		
	a	*b*	*c*	*a*	*b*	*c*
x	1	0	0	1	0	0
y	0	0.2045	0.9789	0	0.5299	0.8480
z	0	0.9789	0.2045	0	0.8480	0.5299

A comparison of the experimental ZFS patterns with those calculated from the distortions of the Ba and Zn sites does not lead to a satisfactory agreement. For a power law dependence of $\bar{b}_2$ with exponents of 7 and 4* the *a*-axis is found to coincide with *z* and *y* resp. for Zn and Ba sites. *x* is 25 and 21° from *b* for Zn and 59 and 58° resp. from *b* for the Ba sites. Thus also a further reduction of the exponent does not result in significantly better agreement of the orientations. While considerable local relaxation may alter the local geometry for Ni^{2+} on the larger Ba sites, the ionic radii of Ni^{2+} and Zn^{2+} are sufficiently similar to make larger relaxations unlikely. It may well be that like in the case of Mn^{2+} [22]** different values of $\bar{b}_2$ have to be used for bridging and nonbridging ligands, but with three adjustable parameters ($\bar{b}_2$(br), $\bar{b}_2$(nbr) and exponent t_2) and possible local relaxations of the Ba site a rigorous test of the validity of the SPM for Ni^{2+} is hardly possible.

The ratios of the axial and rhombic ZFS parameters for Ni^{2+} and Mn^{2+} are ± 22 and ± 21, lower than the value for fluorides in Table 1. The orientations of their principal axes differ considerably, but this could be due to a considerably lower exponent for Ni^{2+} and/or a different ratio of the intrinsic ZFS parameter for bridging and nonbridging

---

* The exponent $t_2 = 4$ is suggested from an analyis of the ZFSs of Ni^{2+} in $CsMgBr_3$ and $CsCdBr_3$ and is in good agreement with the value of 3 obtained for V^{2+} (G. Elbers, Dissertation, Münster 1986). Thus exponents significantly lower than those for the d^5-ions seem typical for non-S-state ions.

** An attempt to explain the ZFS pattern for Mn^{2+} with occupation of Ba sites was unsuccessful although the absence of resolved hyperfine structure due to fluorine even at 20 K would be better compatible with occupation of this site.

ligands. It can thus not be taken as an indication for breakdown of the SPM for Ni^{2+}, but a test of its validity must still await investigation of more suitable systems.

Acknowledgement

This work was supported by grants from the Deutsche Forschungsgemeinschaft.

[1] Y. Yamaguchi, Sol. State Commun. **11,** 1611 (1972).
[2] P. A. Narayana, Phys. Rev. **B 10,** 2676 (1974).
[3] Y. Yamaguchi, J. Phys. Soc. Japan **29,** 1163 (1970).
[4] J. R. Chang, G. L. McPherson, and J. L. Atwood, Inorg. Chem. **14,** 3079 (1975).
[5] G. L. McPherson, T. J. Kistenmacher, and G. D. Stucky, J. Chem. Phys. **52,** 815 (1970).
[6] T. Tri and G. Kuwabara, J. Phys. Soc. Japan **24,** 127 (1968).
[7] G. L. McPherson and K. O. Devaney, Inorg. Chem. **16,** 1565 (1976).
[8] G. L. McPherson, R. C. Koch, and G. D. Stucky, J. Chem. Phys. **60,** 1424 (1974).
[9] K. Katsumata and Y. Yokozawa, J. Phys. Soc. Japan **28,** 1368 (1970).
[10] M. D. Glinchuk, V. E. Goncharuk, D. L. Lyfar, and S. M. Ryabchenko, Sov. Phys. Solid State **18,** 7 (1976).
[11] R. T. Dixon and J. W. Culvahouse, Phys. Rev. **B 3,** 2279 (1971).
[12] R. W. Wilkins and J. W. Culvahouse, Phys. Rev. **B 14,** 1830 (1976).
[13] R. S. Rubins and S. K. Jani, J. Chem. Phys. **66,** 3297 (1977).
[14] R. S. Rubins and K. K. Kwee, J. Chem. Phys. **66,** 3948 (1977).
[15] R. S. Rubins, B. G. Griffin, and R. Burris, J. Chem. Phys. **64,** 3349 (1976).
[16] J. P. Dominicano, W. Sano, K. R. Juraitis, and S. Isotani, J. Phys. Soc. Japan **48,** 1449 (1976).
[17] A. K. Jain and M. Geoffrey, J. Phys. Chem. Solids **44,** 535 (1983).
[18] D. J. Newman and W. Urban, Adv. Phys. **24,** 793 (1975).
[19] S. F. Clare and S. D. Devine, J. Phys. **C 17,** L 581 (1984)
[20] K. A. Müller and W. Berlinger, J. Phys. **C 16,** 6861 (1983).
[21] H. G. von Schnering and P. Bleckmann, Naturwiss. **55,** 342 (1968); H. G. Schnering, private communication.
[22] K. Recker, F. Wallrafen, K. Büscher, and G. Lehmann, Phys. Stat. Sol. (b) **107,** 699 (1981).