Magnetic Anisotropy of Antiferromagnet $(CH_3)_4NMnCl_3$

A. M. Vorotynov, S. G. Ovchinnikov, V. V. Rudenko, and A. N. Sudakov

Kirenskiĭ Institute of Physics, Siberian Division, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia
e-mail: rlm@cc.krascience.rssi.ru

Abstract—The parameters of the electron paramagnetic resonance (EPR) spectra of S ion pairs in diamagnetic crystals are analyzed. A relation between the spin Hamiltonian constants is established for solitary ions and pairs for $(CH_3)_4NCdCl_3 : Mn^{2+}$ crystals. In contrast to solitary ions, an additional contribution (which is a linear function of the exchange field) to the "single-ion" spin Hamiltonian constants appears in the case of pairs. It is shown that anisotropic exchange mechanisms do not play a significant part in the formation of the axial constant of the spin Hamiltonian for this crystal. Some aspects of the method of studying "single-ion" anisotropy predicted by the two-ion model are developed with the help of an isostructural diamagnetic analog with impurity concentration of the paramagnetic ions of a magnetically concentrated substance sufficiently high for observing the EPR spectrum of the pairs. It is found that the microscopic quantities determined partially from the EPR spectra for pairs and solitary Mn^{2+} ions in $(CH_3)_4NCdCl_3$ are in accord with the experimental value of the effective field for the $(CH_3)_4NMnCl_3$ crystal anisotropy which can be described primarily by the dipole and "single-ion" mechanisms of the exchange origin. © 2000 MAIK "Nauka/Interperiodica".

1. The discrepancy between magnetic anisotropy microscopic theories and experiments with compounds containing S ions prompted the computations based on the two-ion models [1]. These computations differ from those carried out using the existing theories of magnetic anisotropy in that they have different values of ionic spins in the excited and the ground states. In this model, anisotropy appears in the third order of the perturbation theory and is a linear function of the exchange interaction energy and a quadratic function of the spin–orbit interaction energy. It was noted in [1] that the "single-ion" anisotropy of the exchange origin, which emerges from the two-ion mechanism, may play a significant role in the description of experimental data. The existence of the "single-ion" exchange anisotropy was studied experimentally in [2, 3].

A detailed theoretical analysis of the two-ion anisotropy was carried out by Moskvin *et al.* [4]. Among other things, they explained the behavior of the of anisotropy energy hematite in a wide temperature range by using the two-ion model. Moskvin *et al.* [4] succeeded in the removal of approximately 23%-discrepancy between the theoretical and experimental curves (describing the antiferromagnetic resonance frequency) in the high-temperature range, which existed according to the results obtained in [5]. The temperature dependence of anisotropy was described in [4] with the help of four fitting parameters (three of which were employed for normalizing the anisotropic exchange contributions).

The available publications on the two-ion mechanism facilitated an advance in understanding the origin of anisotropy in magnetically-ordered crystals with S ions; however, more detailed studies are required to determine anisotropy sources conclusively. A more comprehensive investigation of anisotropy requires a quantitative comparison of the results of calculations with experiment. At the present stage, an attempt of such a comparison can be made using the EPR data for the S-ion pair spectra in diamagnetic analogs isostructural to magnetically-concentrated substances. It is assumed that the equality of lattice parameters is a sufficient condition for identical values and the same symmetry of paired interactions in these crystals. According to Rudenko [6], the necessary condition for the coincidence of the axial constants of the spin Hamiltonian for solitary ions in rhombohedral crystals is the equality of the ratio c_H/a_H of the hexagonal lattice parameters.

However, several conditions must be satisfied for carrying out such investigations.

(1) The relation between the constants in the spin Hamiltonian of pairs and solitary ions should be established, which is not observed in the literature.

(2) The main mechanisms governing the formation of the constants in the spin Hamiltonian for pairs in a given diamagnetic compound should be determined.

(3) A magnetically-concentrated crystal, having an isostructural diamagnetic analog (with close values of the ratio c_H/a_H) and a preferably simple magnetic structure, should be chosen.

(4) The constants of the spin Hamiltonian for pairs in a diamagnetic and a magnetically-concentrated crystal should be put in correspondence.

(5) Reliable and detailed information on the effective anisotropy fields in the magnetically-concentrated crystal and for the constants of the spin Hamiltonian for
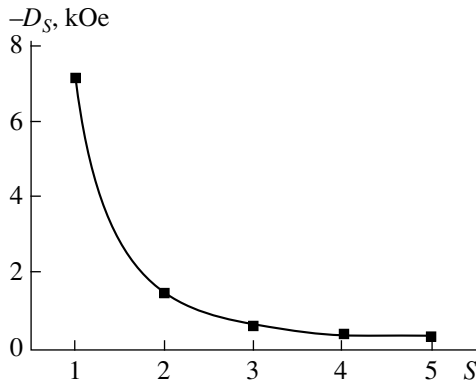
Fig. 1. Dependence of the axial constant D_s of the spin Hamiltonian, which is determined for pairs in $(CH_3)_4NCdCl_3 : Mn^{2+}$ on the total spin S (according to [7]).

pairs and solitary ions of the diamagnetic crystals must be available.

Conditions (3) and (5) are satisfied for $(CH_3)_4NMnCl_3$ and $(CH_3)_4NCdCl_3 : Mn^{2+}$, and the most comprehensive analysis of the EPR spectra for pairs of S ions has been carried out for $(CH_3)_4NCdCl_3 : Mn^{2+}$ crystals [7]. These crystals belong to the hexagonal system with the space group C_{6h}^2. A structural fragment important for EPR studies comprises chains of octahedra formed by Cl^- ions arranged along the sixfold axis of the crystal. The local symmetry of the positions of the Cd^{2+} ions in the octahedra is C_{3i}. The separation between Cd^{2+} ions in a chain is 3.36 Å, while the separation between the chains is 9.13 Å [7]. The lattice parameters are $a_H = 9.138$ Å and $c_H = 6.723$ Å [8]. The compound $(CH_3)_4NMnCl_3$ crystallizes into the $(CH_3)_4NCdCl_3$ structure [8, 9]. The ratio of hexagonal unit cell parameters is $[c_H/a_H] = 0.710$ [9]), which is quite close to the value $[c_H/a_H] = 0.736$ [8]) for $(CH_3)_4NCdCl_3$. The magnetic structure of $(CH_3)_4NMnCl_3$ is that of a quasi-one-dimensional antiferromagnet, the spins lie in the basal plane, the Néel temperature T_N is 0.835 K, and the exchange interaction parameter $[J/k]$ is 13 K.

2. The Hamiltonian for Mn^{2+} paired ions in a $(CH_3)_4NCdCl_3$ crystal in the strong-exchange approximation disregarding the hyperfine interaction can be written in the form [7, 10]

$$\mathcal{H} = g\beta \mathbf{H S} + (J/2)[S(S+1) - S_i(S_i+1) - S_j(S_j+1)]$$
$$+ D_s[S_z^2 - (1/3)S(S+1)], \quad (1)$$

where $\mathbf{H}$ is the external magnetic field; $\mathbf{S} = \mathbf{S}_i + \mathbf{S}_j$ is the spin operator; S is the total spin which can assume the values $S = S_i + S_j, S_i + S_j - 1, \ldots, S_i - S_j; S_i = S_j = 5/2$; $D_s = 3\alpha_s D_e + \beta_s D_c$; $\alpha_s = (1/2)\{[S(S+1) - 4S_i(S_i+1)]/[(2S-1)(2S+3)]\}$; $\beta_s = \{[3S(S+1) - 3 - 4S_i(S_i+1)]/[(2S-1)(2S+3)]\}$; $D_e = D_E + D_{dip}$; D_E being the

anisotropic exchange constant; $D_{dip} = -g^2\beta^2/r_{ij}^3$; and D_c the "single-ion" constant. The Hamiltonian (1) can describe the experimental results for crystals with a dipole and single-ion anisotropy (including that of the exchange origin) and with an anisotropic exchange described by a second-order invariant in the spin operators. However, the fourth-order anisotropic exchange terms calculated in [1, 4] are not taken into account in (1).

Expression (1) shows that each multiplet of a pair with spin S is in an exchange field which can be directed along the z axis of the reference frame ($z \parallel C_6$) if $H = H_z$. This means that the quantization axis for the total spin moment is directed along z. With this orientation of the exchange field, each ionic spin (for multiplets) will be regarded as lying in the xz plane and deflected from the x axis towards the z axis. In this case, the expression for the exchange field can be written as $H_z^{ex} = -[(1/g\beta)\partial E_s/\partial S_z] = -(J/g\beta)(S_z + 1/2) = -(J/g\beta)(S + 1/2)$, where the E_s are exchange energy levels of the Hamiltonian (1).

The experimental results [7] for this crystal are plotted in the form of a graph in Fig. 1.

We present D_s in the form $D_s = 3\alpha_s D'_{dip} + \beta_s(P_1 + P_2S)$, where P_k are fitting parameters ($k = 1, 2$). The parameters P_1 and P_2 are used for describing the linear dependence of the "single-ion" constant D_c of the spin Hamiltonian on the exchange field. A dependence of this type was obtained in [2, 3] for the system of magnetically concentrated crystals $MnCO_3$, $FeBO_3$, and α-Fe_2O_3. The expression for D'_{dip} is written taking into account additional dipole contributions emerging as a result of deviation from the point model and delocalization of the electrons of paramagnetic ions due to covalent effects [11]. It is also assumed that exchange–striction interactions [11] do not play any significant role in this crystal. Note that the exchange–striction model was used in [7, 12] for describing the experimental data obtained for a $(CH_3)_4NCdCl_3 : Mn^{2+}$ crystal. However, the fitting parameters used by the authors of [7, 12] led to a lattice distortion upon a change in the spin number S that was too strong.

Let us estimate D'_{dip} from the experimental data for D_s. Since β_3 has a small value, we can write $D'_{dip} \approx [D_3/3\alpha_s] = -398.1$ Oe. Fitting the value of D_s with the help of the parameters P_1 and P_2 by the least square technique, we obtain $D'_{dip} = \{[D_3 - \beta_3(P_1 + P_2S)]/3\alpha_s\} = -391.4$ Oe. Expressing the "single-ion" constant from D_s and plotting $D_c = P'_1 + P'_2 S'$ as a function of H_z^{ex} (S') ($S' = S + 1/2$) with a subsequent fitting, we find that the experimental points indeed fall well on the theoretical dependence that is a linear function (Fig. 2) with the parameters $P'_1 = 619.8 \pm 25$ Oe and $P'_2 = -110.2 \pm 7$ Oe.

The parameter P_1' can be obtained by extrapolating the curve in Fig. 2 to zero exchange field for the multiplets of a pair and should be equal to the sum of the constant $D_{cf} = 43.9$ Oe of the spin Hamiltonian for a solitary ion [7] and the contribution D_{c0} due to the distortion of the $(CH_3)_4NCdCl_3$ lattice by "foreign" pair. In order to compare the effect of lattice distortions produced by a pair on D_{c0}, we consider the slopes of the linear dependence of the spin Hamiltonian constant for a solitary Fe^{3+} ion in $GaBO_3$, $InBO_3$, $LuBO_3$, and $ScBO_3$ crystals [6] and D_{c0} relative to c_H/a_H. We shall assume that local lattice distortions can also be described by the parameter c_H/a_H. For the most precisely determined value of $\Delta(c_H/a_H)$, for D_{c0}, we obtain $\Delta(c_H/a_H)[(D_{cf} - P_1')/\Delta(c_H/a_H)] = -2.2 \times 10^4$ Oe. For the set of diamagnetic crystals investigated by us, we have $[\Delta D_{cf}/\Delta(c_H/a_H)] = -2.6 \times 10^3$ Oe. These quantities have the same sign and can be comparable even for the actual lattice distortions in $(CH_3)_4NCdCl_3$.

The obtained results can be used for calculating the magnetic anisotropy of a $(CH_3)_4NMnCl_3$ crystal. The "single-ion" constant of the spin Hamiltonian for a magnetically concentrated crystal can be written in the form

$$D_{mc} = D_{cf} + D_{ex} = D_c(H_{zn}^{ex}) - D_{c0}.$$

Here, D_{ex} is the contribution of the two-ion mechanism to the "single-ion" constant of the spin Hamiltonian for the magnetically-concentrated crystal and H_{zn}^{ex} is the exchange field at the multiplets of a pair, which corresponds to definite parameters of the magnetically-concentrated crystal.

In order to find the relation between the exchange energy parameters of a magnetically-concentrated crystal in the molecular field approximation and of a pair, we carry out the following calculations. We write the exchange interaction energy of the ith ion for a magnetically-concentrated crystal at $T = 0$ K in the form $E_{mc}(T = 0\ K) = -nJS_iS_j$, where n is the number of the magnetically-active nearest neighbors of the ith ion. Putting $n = n_0 = 1$ and equating

$$E_{mc}(T = 0, n_0) = E_S, \qquad (2)$$

we establish the value of the effective spin number S_{n0} for a pair, which corresponds to the energy $E_{mc}(T = 0)$ of the lower level for the ith ion in the magnetically-concentrated crystal. The solution of the quadratic equation (2) gives the value of the spin number $S_{n0} = 1.8$. Further, carrying out the summation over the pair bonds of the ith ion, we find the exchange energy $E_{mc}(T = 0) = nE_s(S_{n0})$ of interaction of the ith ion with its nearest neighbors for the magnetically-concentrated crystal at $T = 0$ K in terms of S_i, S_j, S_{n0}, and n. The energy $E_{mc}(T = 0)$ corresponds to the exchange field $H_{zn}^{ex} = -2.3n(J/g\beta)$. For the
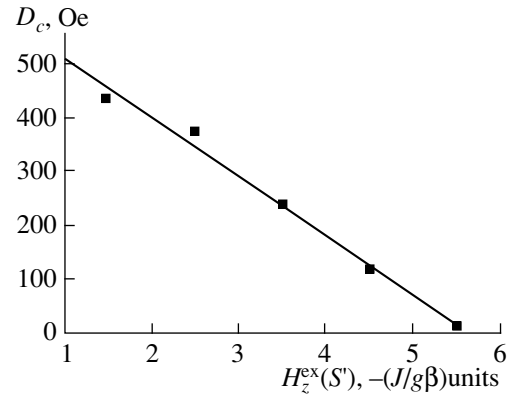

Fig. 2. Dependence of the "single-ion" constant D_c of the spin Hamiltonian on the exchange field for spin multiplets of a pair.

corresponding exchange field of the $(CH_3)_4NMnCl_3$ crystal, the value of the "single-ion" constant of the spin Hamiltonian can be defined as $D_{mc} = [D_{cf} + P_2'|H_{zn}^{ex}|/(J/g\beta)] = D_{cf} - 0.00115|H_{zn}^{ex}|$. The slope calculated for the dependences for $MnCO_3$, $FeBO_3$, and α-Fe_2O_3 crystals [2, 3] is given by $\tan\alpha = [D_{ex}/H_E'] = -0.00048$. The obtained values of the slopes of the straight lines describing the constants of the spin Hamiltonian as functions of the exchange field are quite close, indicating that the obtained results reflect the actual pattern of the interaction.

Thus, the results presented above lead to the following conclusions.

(1) The "single-ion" constant of the spin Hamiltonian in zero exchange field at the multiplets of a pair is equal to the constant of a solitary ion plus the contribution D_{c0} due to distortions emerging when a "foreign" pair appears in a diamagnetic crystal.

(2) In contrast to solitary ions, pairs acquire an additional contribution to the "single-ion" constant of the spin Hamiltonian, which is a linear function of exchange field. This contribution is determined by the two-ion mechanism.

(3) The anisotropic exchange mechanisms calculated and estimated in [4] as very strong for hematite do not play any significant role in the formation of the spin Hamiltonian constant in $(CH_3)_4NCdCl_3$: Mn^{2+} and $(CH_3)_4NMnCl_3$ crystals.

Taking into account the uniaxial anisotropy, we can write the thermodynamic potential in the form

$$\Phi = (1/2)Bm^2 + (1/2)al_z^2, \qquad (3)$$

where $\mathbf{m} = (\mathbf{M}_1 + \mathbf{M}_2)/M$, $\mathbf{l} = (\mathbf{M}_1 - \mathbf{M}_2)/M$, and $M = 2|\mathbf{M}_1| = 2|\mathbf{M}_2|$.

The contribution of the dipole interaction at $T = 0$ K is estimated as $H_{A,dip} = 5.39$ kOe [13]. In accordance with (3) and [6], the "single-ion" contribution to the

uniaxial anisotropy constant at $T = 0$ K can be written in the form

$$a_{sf}(0) = 2NS_i(S_i - 1/2)[D_{cf} + P'_2|H^{ex}_{zn}|/(J/g\beta)],$$

where the spin Hamiltonian constants are expressed in energy units. Substituting the available data, we find the contributions of the single-ion and two-ion exchange mechanisms to $H_{A,cf} = [a_{cf}(0)/M(0)] = 0.18$–$2.02 = -1.84$ kOe, which gives $H_A(0) = H_{A,cf}(0) + H_{A,\,dip}(0) = 3.55$ kOe. The experimental results obtained for $(CH_3)_4NMnCl_3$ by using various methods and compiled in [14] give the following values of $H_A(0)$: 3.31, 3.89, and 4.73 kOe, which are, on the average, in good agreement with the estimate presented above.

3. It should be noted, in conclusion, that the expression for the magnetic anisotropy constant can be used for any magnetically-concentrated crystal of an appropriate symmetry, which contains paramagnetic Mn^{2+} ions; the pairwise anisotropic interactions between these ions in the diamagnetic analog are described by the dipole and the "single-ion" constants of the spin Hamiltonian. It is also assumed that the exchange–striction contribution to these constants is insignificant.

ACKNOWLEDGMENTS

REFERENCES

1. A. E. Nikiforov, V. Ya. Mitrofanov, and A. N. Men, Phys. Status Solidi B **45** (1), 65 (1971).
2. O. A. Bayukov and V. V. Rudenko, Preprint No. 669F (Institute of Physics, Siberian Division, Russian Academy of Sciences, Krasnoyarsk, 1990).
3. O. A. Bayukov and V. V. Rudenko, Fiz. Tverd. Tela (St. Petersburg) **34**, 2665 (1992) [Sov. Phys. Solid State **34**, 1428 (1992)].
4. A. S. Moskvin, I. G. Bostrem, and M. A. Sidorov, Zh. Éksp. Teor. Fiz. **104**, 2499 (1993) [JETP **77**, 127 (1993)].
5. K. S. Aleksandrov, L. N. Bezmaternykh, G. V. Kozlov, *et al.*, Zh. Éksp. Teor. Fiz. **92**, 1042 (1987) [Sov. Phys. JETP **65**, 591 (1987)].
6. V. V. Rudenko, Author's Abstract of Candidate's Dissertation (Simferopol', 1983).
7. M. Heming, G. Lehmann, H. Mosebach, and E. Siegel, Solid State Commun. **44** (4), 543 (1982).
8. B. Morosin, Acta Crystallogr. B **28**, 2303 (1972).
9. B. Morosin and E. J. Graeber, Acta Crystallogr. **23** (5), 766 (1967).
10. J. Owen, J. Appl. Phys., Suppl. **32** (3), 213S (1961).
11. E. A. Harris, J. Phys. C **5**, 338 (1972).
12. S. N. Martynov and S. B. Petrov, Phys. Status Solidi B **149**, K41 (1988).
13. A. I. U. Heilmann, J. K. Kjems, Y. Endoh, *et al.*, Phys. Rev. B **24**, 3939 (1981).
14. M. E. Gouvea and A. S. T. Pires, Phys. Rev. B **34**, 306 (1986).

Translated by N. Wadhwa