

## Exchange Interactions within Nearest-Neighbor Cr<sup>3+</sup> Pairs in Chromium-Doped Spinel ZnGa<sub>2</sub>O<sub>4</sub>

J. C. M. Henning and J. P. M. Damen

*Philips Research Laboratories, N. V. Philips Gloeilampenfabrieken, Eindhoven, The Netherlands*

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Exchange interactions within nearest-neighbor Cr<sup>3+</sup> pairs in Cr-doped spinel ZnGa<sub>2</sub>O<sub>4</sub> are studied by means of electron spin resonance. Apart from isotropic exchange, biquadratic and anisotropic terms are needed for an adequate description of the experimental results:  $\mathcal{H}_{\text{ex}} = -J\vec{s}_1 \cdot \vec{s}_2 + j(\vec{s}_1 \cdot \vec{s}_2)^2 + A[\vec{s}_1 \cdot \vec{s}_2 - 3(\vec{s}_1 \cdot \vec{r}_{12})(\vec{s}_2 \cdot \vec{r}_{12})/r_{12}^2]$ . The coefficients are found to be  $\bar{s} J/k = (-16.5 \pm 1.0)^\circ\text{K}$ ,  $j/k = (-2.5 \pm 1.0)^\circ\text{K}$ , and  $A = +0.016 \pm 0.001 \text{ cm}^{-1}$ . Since dipole-dipole interactions would lead to  $A_{\text{dip}} = +0.067 \text{ cm}^{-1}$ , it follows that a negative anisotropic exchange counteracts the  $d-d$  interaction to an appreciable amount. The large negative biquadratic exchange is explained in terms of Kittel's exchange-striction mechanism.

Magnetic ordering in spinels ( $AB_2O_4$ ) with predominant  $B-B$  interactions is generally ill understood.<sup>1</sup> The large difference between the asymptotic Curie temperature ( $\Theta = -380^\circ\text{K}$ ) and the Néel point ( $T_N = 15^\circ\text{K}$ ) in ZnCr<sub>2</sub>O<sub>4</sub><sup>2</sup> and MgCr<sub>2</sub>O<sub>4</sub><sup>3</sup> suggests that long-range ordering ( $T_N$ ) is induced by non-nearest-neighbor interactions, whereas the large value of  $\Theta$  is mainly due to nearest-neighbor interactions. The relevance of more distant interactions to the explanation of complicated spin configurations has been pointed out by several authors.<sup>4-7</sup> In particular Dwight and Menyuk,<sup>7</sup> using the Luttinger-Tisza method, were able to show that the observed helical spin structure<sup>4</sup> of ZnCr<sub>2</sub>Se<sub>4</sub> is stable if and only if the values of six interaction parameters fall inside a rather limited region. A similar treatment for the more complicated spin structure of MgCr<sub>2</sub>O<sub>4</sub><sup>8</sup> has not yet been attempted. An independent determination of the  $B-B$  exchange interaction strengths seems highly desirable. It is well known<sup>9</sup> that the electron-spin-resonance (ESR) method is able to provide direct and detailed information not only about first-neighbor interactions but also about more distant interactions.

In this paper we report preliminary results of an ESR investigation on the Cr<sup>3+</sup>-doped cubic normal spinel ZnGa<sub>2</sub>O<sub>4</sub>. We have chosen ZnGa<sub>2</sub>O<sub>4</sub> as a host lattice because of the near perfect match in ionic radii of Cr<sup>3+</sup> (0.63 Å) and Ga<sup>3+</sup> (0.62 Å). Therefore, substitution of Cr<sup>3+</sup> for Ga<sup>3+</sup> is expected to cause only small distortions in the lattice. This reasoning is substantiated by the close proximity of the lattice parameters of ZnGa<sub>2</sub>O<sub>4</sub> and ZnCr<sub>2</sub>O<sub>4</sub>, viz,  $a = 8.335$  and  $8.327$  Å, respectively.

Cr-doped ZnGa<sub>2</sub>O<sub>4</sub> single crystals were grown by a method described earlier.<sup>10</sup> Red transparent crystals were obtained with a spectrochemically determined impurity content of  $5 \times 10^{-5}$  g at. Rh,

$1 \times 10^{-3}$  g at. Pt,  $9 \times 10^{-5}$  g at. Ni,  $1 \times 10^{-4}$  g at. Fe, and  $2 \times 10^{-4}$  g at. Cu per mole ZnGa<sub>2</sub>O<sub>4</sub>. The chromium concentration used in these investigations was  $5 \times 10^{-2}$  g at./mole.

The ESR spectrum of single Cr<sup>3+</sup> ions at  $B$  sites can be described<sup>10,11</sup> by an axial spin Hamiltonian

$$\mathcal{H}_i = g_{\parallel} \mu_B H_{zi} S_{zi} + g_{\perp} \mu_B (H_{xi} S_{xi} + H_{yi} S_{yi}) + D [s_{zi}^2 - \frac{1}{3} s_i(s_i + 1)], \quad (1)$$

with  $s_i = \frac{3}{2}$ ,  $g_{\parallel} = 1.9776 \pm 0.0003$ ,  $g_{\perp} = 1.9867 \pm 0.0007$ , and  $D = +0.523 \pm 0.002 \text{ cm}^{-1}$ . The center axes  $z_i$  ( $i = 1, \dots, 4$ ) are directed along the four local trigonal  $\langle 111 \rangle$  axes. In crystals containing 1–5 at. % Cr, additional weak lines appear in the spectrum, which on account of their Cr-concentration dependence are ascribed to chromium pairs.

The spin Hamiltonian for a Cr-Cr pair

$$\mathcal{H}_{\text{pair}} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{\text{ex}} \quad (2)$$

contains, in addition to the sum of two single-ion Hamiltonians  $\mathcal{H}_i$  of the form of (1), an interaction term  $\mathcal{H}_{\text{ex}}$ :

$$\mathcal{H}_{\text{ex}} = -J\vec{s}_1 \cdot \vec{s}_2 + j(\vec{s}_1 \cdot \vec{s}_2)^2 + A [\vec{s}_1 \cdot \vec{s}_2 - 3(\vec{s}_1 \cdot \vec{r}_{12})(\vec{s}_2 \cdot \vec{r}_{12})/r_{12}^2]. \quad (3)$$

Here, the isotropic bilinear (Heisenberg) exchange has been augmented with biquadratic and anisotropic terms. The biquadratic term is necessary for a correct description of the separations between the spin multiplets<sup>12</sup> (if  $s_1, s_2 > \frac{1}{2}$ ). The symmetric anisotropic exchange is approximated by the pseudodipolar form,<sup>13</sup> which contains the classical point dipole-dipole interaction:

$$A = A_d + A_{\text{an}} = g^2 \mu_B^2 / r_{12}^3 + A_{\text{an}}. \quad (4)$$

If we confine our attention to nearest-neighbor (nn)

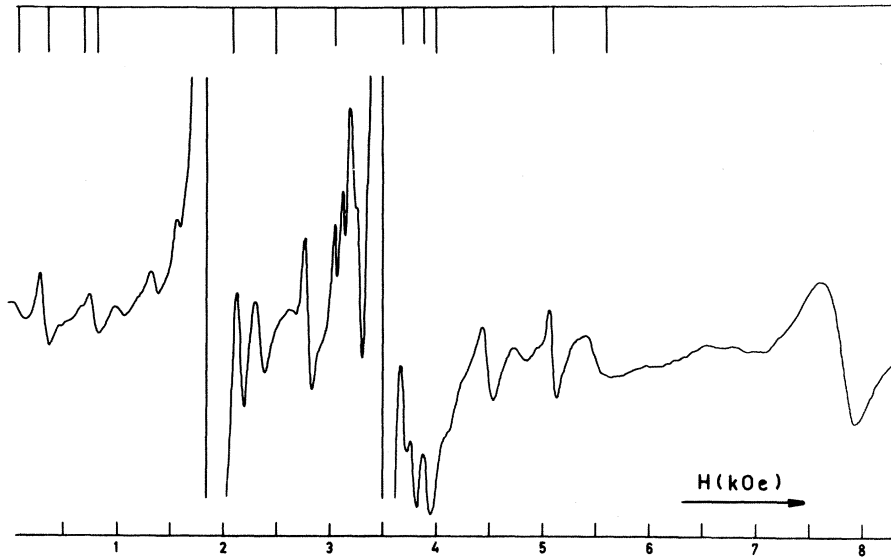


FIG. 1. Lower trace: part of ESR spectrum of  $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$  at  $T=77^\circ\text{K}$ ,  $\vec{H} \parallel [111]$ ,  $\nu=9684$  MHz. Strong lines at 1845, 3475, and 7755 Oe are due to single  $\text{Cr}^{3+}$  ions. Upper trace: theoretical positions of  $S=3$  (longer bars) and  $S=2$  (shorter bars) transitions of nn pairs with  $\vec{z}_1 \parallel [111] \parallel \vec{H}$ .

pairs, the assumption  $J \gg D$ ,  $g \mu_B H$  is reasonable and the total spin  $S$  will be a good quantum number. Then  $\mathcal{H}_{\text{pair}}$  may be rewritten as

$$\begin{aligned} \mathcal{H}_{\text{pair}} = & -\frac{1}{2} JS(S+1) + \frac{1}{4} jS(S+1) \\ & \times [S(S+1) - 2s_1(s_1+1) - 2s_2(s_2+1)] \\ & + D[s_{z_1}^2 + s_{z_2}^2 \cos^2 \gamma + (s_{z_2} s_{x_2} + s_{x_2} s_{z_2}) \sin \gamma \cos \gamma \\ & + s_{x_2}^2 \sin^2 \gamma] + g \mu_B \vec{H} \cdot \vec{S} + A [\vec{s}_1 \cdot \vec{s}_2 - 3(\vec{s}_1 \cdot \vec{r}_{12}) \\ & \times (\vec{s}_2 \cdot \vec{r}_{12}) / r_{12}^2], \quad (5) \end{aligned}$$

where  $g = \frac{1}{2}(g_{\parallel} + g_{\perp})$ . The quantization axis is chosen along the center axis  $z_1$  of ion No. 1, where  $\gamma$  is the angle between the center axes of both ions, and for first neighbors,  $\gamma = 70^\circ 32'$ .

The two leading terms in Eq. (5) give rise to the four multiplets  $S=3, 2, 1, 0$  with energies  $-6J-9j$ ,  $-3J-27/2j$ ,  $-J-13/2j$ , and 0, respectively. At X-band frequencies ( $\nu \approx 9700$  MHz) only transitions within the multiplets  $S=3$  and  $S=2$  are observed. To first approximation the positions of these transitions are independent of  $J$  and  $j$ , and can be calculated from the single-ion  $D$ ,  $g_{\parallel}$  and  $g_{\perp}$  values, the only adjustable parameter being  $A$ .

A typical spectrum for  $\vec{H} \parallel [111]$  and  $T=77^\circ\text{K}$  is presented in Fig. 1. In Table I the calculated line positions for those nn pairs which have  $\vec{z}_1 \parallel [111] \parallel \vec{H}$  are compared with experiment. Satisfactory agreement is obtained with  $A = +0.016 \pm 0.001 \text{ cm}^{-1}$ . Since dipole-dipole interaction would lead to  $A_d = +0.067 \text{ cm}^{-1}$ , this result means that  $d-d$  interaction is counteracted to a large extent by pseudo-dipolar anisotropic exchange:  $A_{\text{an}} = -0.051 \text{ cm}^{-1}$ . The observed  $A$  value is sufficiently different from the  $A$  value of second neighbors ( $A \approx A_d = 0.012 \text{ cm}^{-1}$ )

to allow an unambiguous assignment to nn pairs to be made.

The values of  $J$  and  $j$  are derived from the temperature dependence of the resonance intensities.<sup>9</sup> The data for transitions within  $S=2$  and  $S=3$  are incompatible unless a fairly considerable biquadratic exchange term is introduced. The best fit gives  $J/k = (-16.5 \pm 1)^\circ\text{K}$  and  $j/k = (-2.5 \pm 1)^\circ\text{K}$ .

Thus, for nearest neighbors, the bilinear ex-

TABLE I. Experimental and theoretical positions (in Oe) of ESR transitions within the  $S=3$  and  $S=2$  multiplets.  $\vec{H} \parallel [111] \parallel z_1$ ,  $T=77^\circ\text{K}$ ,  $\nu=9684$  MHz. Transitions within  $S=1$  are not observable at this frequency.

$S$	$M \rightarrow M-1$	$H(\text{theory})^a$	$H(\text{expt})$	$T_m^b$
3	$3 \rightarrow 2$	$750 \pm 25$	$730 \pm 20$	$63 \pm 3$
3	$2 \rightarrow 1$	$400 \pm 100$	$300 \pm 10$	$63 \pm 3$
		$2500 \pm 50$	$2780 \pm 10$	$63 \pm 3$
3	$1 \rightarrow 0$	$840 \pm 50$	$770 \pm 10$	$63 \pm 3$
		$2050 \pm 50$	$2150 \pm 10$	$63 \pm 3$
		$3950 \pm 50$	$4440 \pm 10$	$63 \pm 3$
3	$0 \rightarrow -1$	$5100 \pm 25$	$5070 \pm 10$	$63 \pm 3$
3	$-1 \rightarrow -2$	$100 \pm 100$	$60 \pm 20$	$63 \pm 3$
3	$-2 \rightarrow -3$	$5600 \pm 50$	$5500 \pm 40$	$63 \pm 3$
2	$2 \rightarrow 1$	$3850 \pm 25$	$3890 \pm 10$	c
2	$1 \rightarrow 0$	$3660 \pm 25$	$3673 \pm 5$	c
2	$0 \rightarrow -1$	$3400 \pm 25$	d	
2	$-1 \rightarrow -2$	$3036 \pm 25$	$3041 \pm 5^e$	$40 \pm 3$

<sup>a</sup>With  $A = (+0.016 \pm 0.001) \text{ cm}^{-1}$ .

<sup>b</sup> $T_m$  = temperature (in  $^\circ\text{K}$ ) at which maximum intensity occurs.

<sup>c</sup>Composite lines.

<sup>d</sup>Coincides with strong single-ion absorption.

<sup>e</sup>Another  $S=2$ ,  $-1 \rightarrow -2$  transition, due to nn pairs with  $\angle(\vec{z}_1, \vec{H}) = \angle(\vec{z}_2, \vec{H}) = 70^\circ 32'$ , has been observed  $H = 3120 \pm 5$  Oe. The temperature dependence of its intensity is identical with that of the 3041-Oe line.

change is found to be negative (antiferromagnetic), as might be intuitively deduced from the strongly negative value of  $\Theta$  of the isomorphous compound  $\text{ZnCr}_2\text{O}_4$ . Our result throws doubt on the positive  $J$  value found by Blazey<sup>14</sup> from the fluorescence spectrum of Cr-doped  $\text{ZnAl}_2\text{O}_4$  powders.

A negative coefficient  $j$  of the biquadratic exchange is not uncommon<sup>15,16</sup> but is incompatible with a fourth-order Anderson transfer mechanism.<sup>17</sup> The magnitude of the effect, too, is in disagreement with Anderson's<sup>18</sup> estimate:

$$j/k \simeq J^2/kU = 0.003 \text{ }^\circ\text{K}.$$

An alternative mechanism, leading to a negative biquadratic term in the spin Hamiltonian is the exchange magnetostriction discussed by Kittel.<sup>19</sup> This effect is most effective if  $J$  has a strong dependence on the Cr-Cr separation  $r_0$ :

$$j = -\frac{1}{2}(\rho^2/cr_0) \quad , \quad (6)$$

where  $\rho = dJ/dr_0$  and  $c$  is the elastic stiffness. Motida and Miyahara<sup>20</sup> recently pointed out that  $\rho$  is rather large for  $90^\circ$  Cr-Cr interactions as a consequence of a subtle balance between negative direct<sup>21</sup> (Cr-Cr) exchange and positive indirect (Cr-O-Cr) exchange interactions. A plot<sup>20</sup> of  $\Theta$  vs  $r_0$  for the oxides  $\text{LiCrO}_2$ ,  $\text{ZnCr}_2\text{O}_4$ ,  $\text{MgCr}_2\text{O}_4$ ,  $\text{NaCrO}_2$ ,  $\text{HCrO}_2$ ,  $\text{DCrO}_2$ ,  $\text{CuCrO}_2$ , and  $\text{CdCr}_2\text{O}_4$  gives  $d\Theta/dr_0 = 35 \times 10^{10} \text{ }^\circ\text{K/cm}$ , which leads to  $\rho = 64 \times 10^{-7} \text{ erg/cm}$  if the assumption is made that  $\Theta$  is mainly determined by nn interactions. With  $c \simeq 20 \times 10^{11} \text{ dyn/cm}^2$  and  $r_0 = 2.94 \times 10^{-8} \text{ cm}$  we finally obtain  $j/k = -2.5 \text{ }^\circ\text{K}$ , in excellent agreement with experiment.

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<sup>1</sup>F. K. Lotgering, reported at the International Conference on Magnetism, Grenoble, 1970 [J. Phys. Radium (to be published)].

<sup>2</sup>J. M. Hastings and L. M. Corliss, reported in J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience, New York, 1963), p. 148.

<sup>3</sup>G. Blasse and J. F. Fast, Philips Res. Rept. 18, 393 (1963).

<sup>4</sup>R. Plumier, Compt. Rend. Acad. Sci. Paris 260, 3348 (1965).

<sup>5</sup>F. K. Lotgering, Solid State Commun. 3, 347 (1965).

<sup>6</sup>P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin, Phys. Rev. 151, 367 (1966).

<sup>7</sup>K. Dwight and N. Menyuk, Phys. Rev. 163, 435 (1967).

<sup>8</sup>R. Plumier, Compt. Rend. Acad. Sci. Paris 267, 98 (1968).

<sup>9</sup>See, for instance, D. M. S. Bagguley and J. Owen, Rept. Progr. Phys. 20, 304 (1957); J. Owen, J. Appl. Phys. 32, 213S (1961); 33, 355S (1962).

<sup>10</sup>H. van den Boom, J. C. M. Henning, and J. P. M.

Damen, Solid State Commun. 8, 717 (1970).

<sup>11</sup>H. M. Kahan and R. M. Macfarlane, Bull. Am. Phys. Soc. 15, 249 (1970).

<sup>12</sup>K. H. W. Stevens, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. 1, p. 1.

<sup>13</sup>J. H. van Vleck, Phys. Rev. 52, 1178 (1937).

<sup>14</sup>K. W. Blazey, Solid State Commun. 4, 541 (1966).

<sup>15</sup>E. A. Harris and J. Owen, Phys. Rev. Letters 11, 9 (1963).

<sup>16</sup>H. Ikeda, I. Kimura, and N. Uryu, J. Chem. Phys. 48, 4809 (1968).

<sup>17</sup>R. P. van Stapele (private communication).

<sup>18</sup>P. W. Anderson, in Ref. 12, Vol. I, p. 25.

<sup>19</sup>C. Kittel, Phys. Rev. 120, 335 (1960).

<sup>20</sup>K. Motida and S. Miyahara, J. Phys. Soc. Japan 28, 1188 (1970).

<sup>21</sup>J. B. Goodenough, Phys. Rev. 117, 1442 (1960); J. Kanamori, J. Phys. Chem. Solids 10, 87 (1959).