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Exchange Interactions within Nearest-Neighbor Cr^{3+} Pairs in Chromium-Doped Spinel $ZnGa_2O_4$

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^{3+} pairs in Cr-doped spinel $ZnGa_2O_4$ 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: $\mathcal{H}_{ex} = -J\vec{s}_1\cdot\vec{s}_2 + j(\vec{s}_1\cdot\vec{s}_2)^2 + A[\vec{s}_1\cdot\vec{s}_2 - 3(\vec{s}_1\cdot\vec{r}_{12})(\vec{s}_2\cdot\vec{r}_{12})/r_{12}^2]$. The coefficients are found to be $\vec{s}$ $J/k = (-16.5\pm1.0)$ °K, $j/k = (-2.5\pm1.0)$ °K, and $A = +0.016\pm0.001\ \text{cm}^{-1}$. Since dipole-dipole interactions would lead to $A_{dip} = +0.067\ \text{cm}^{-1}$, 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.[1] The large difference between the asymptotic Curie temperature ($\Theta = -380$ °K) and the Néel point ($T_N = 15$ °K) in $ZnCr_2O_4$ [2] and $MgCr_2O_4$ [3] suggests that long-range ordering (T_N) is induced by non-nearest-neighbor interactions, whereas the large value of Θ 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.[4–7] In particular Dwight and Menyuk,[7] using the Luttinger-Tisza method, were able to show that the observed helical spin structure[4] of $ZnCr_2Se_4$ 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 $MgCr_2O_4$ [8] has not yet been attempted. An independent determination of the *B-B* exchange interaction strengths seems highly desirable. It is well known[9] 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^{3+}-doped cubic normal spinel $ZnGa_2O_4$. We have chosen $ZnGa_2O_4$ as a host lattice because of the near perfect match in ionic radii of Cr^{3+} (0.63 Å) and Ga^{3+} (0.62 Å). Therefore, substitution of Cr^{3+} for Ga^{3+} is expected to cause only small distortions in the lattice. This reasoning is substantiated by the close proximity of the lattice parameters of $ZnGa_2O_4$ and $ZnCr_2O_4$, viz, $a = 8.335$ and 8.327 Å, respectively.

Cr-doped $ZnGa_2O_4$ single crystals were grown by a method described earlier.[10] Red transparent crystals were obtained with a spectrochemically determined impurity content of 5×10^{-5} g at. Rh, 1×10^{-3} g at. Pt, 9×10^{-5} g at. Ni, 1×10^{-4} g at. Fe, and 2×10^{-4} g at. Cu per mole $ZnGa_2O_4$. The chromium concentration used in these investigations was 5×10^{-2} g at./mole.

The ESR spectrum of single Cr^{3+} ions at *B* sites can be described[10,11] by an axial spin Hamiltonian

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

with $s_i = \frac{3}{2}$, $g_\parallel = 1.9776\pm0.0003$, $g_\perp = 1.9867\pm0.0007$, and $D = +0.523\pm0.002\ \text{cm}^{-1}$. The center axes z_i ($i = 1, \ldots, 4$) 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

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

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

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

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[12] (if $s_1, s_2 > \frac{1}{2}$). The symmetric anisotropic exchange is approximated by the pseudodipolar form,[13] which contains the classical point dipole-dipole interaction:

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

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

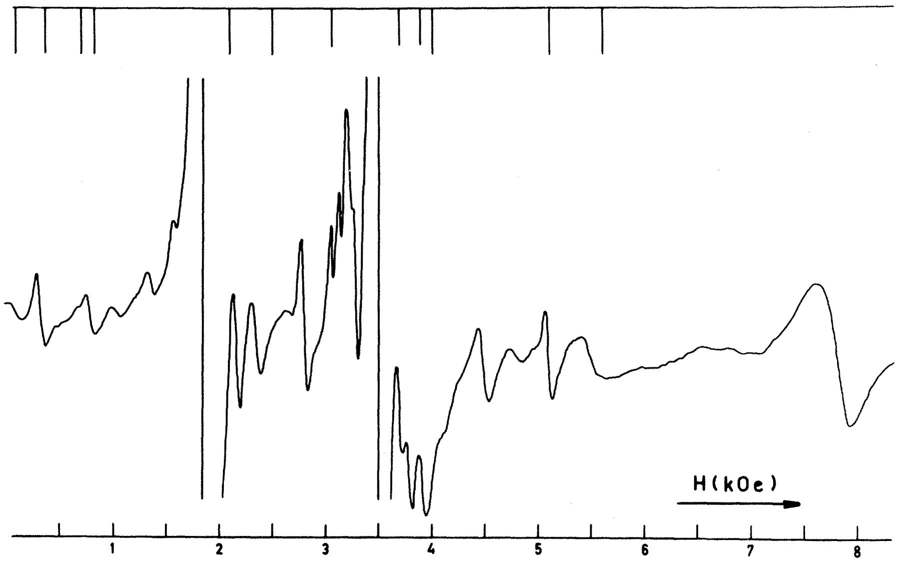

FIG. 1. Lower trace: part of ESR spectrum of $ZnGa_2O_4:Cr^{3+}$ at $T = 77$ °K, $\vec{H} \parallel [111]$, $\nu = 9684$ MHz. Strong lines at 1845, 3475, and 7755 Oe are due to single Cr^{3+} ions. Upper trace: theoretical positions of $S = 3$ (longer bars) and $S = 2$ (shorter bars) transitions of nn 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

$$\mathcal{H}_{\text{pair}} = -\tfrac{1}{2} JS(S+1) + \tfrac{1}{4} jS(S+1) \times [S(S+1) - 2s_1(s_1+1) - 2s_2(s_2+1)]$$
$$+ D[s_{z1}^2 + s_{z2}^2 \cos^2\gamma + (s_{z2}s_{x2} + s_{x2}s_{z2}) \sin\gamma\cos\gamma + s_{x2}^2 \sin^2\gamma] + g\mu_B \vec{H}\cdot\vec{S} + A[\vec{s}_1\cdot\vec{s}_2 - 3(\vec{s}_1\cdot\vec{r}_{12}) \times (\vec{s}_2\cdot\vec{r}_{12})/r_{12}^2], \qquad (5)$$

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

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 $T = 77$ °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 $A = +0.016 \pm 0.001$ cm^{-1}. Since dipole-dipole interaction would lead to $A_d = +0.067$ cm^{-1}, this result means that d-d interaction is counteracted to a large extent by pseudodipolar anisotropic exchange: $A_{an} = -0.051$ cm^{-1}. The observed A value is sufficiently different from the A value of second neighbors ($A \approx A_d = 0.012$ 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.[9] 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 $J/k = (-16.5 \pm 1)$ °K and $j/k = (-2.5 \pm 1)$ °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. $\vec{H} \parallel [111] \parallel z_1$, $T = 77$ °K, $\nu = 9684$ MHz. Transitions within $S = 1$ are not observable at this frequency.

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

[a] With $A = (+0.016 \pm 0.001)$ cm^{-1}.

[b] T_m = temperature (in °K) at which maximum intensity occurs.

[c] Composite lines.

[d] Coincides with strong single-ion absorption.

[e] Another $S = 2$, $-1 \to -2$ transition, due to nn pairs with $\angle(\vec{z}_1, \vec{H}) = \angle(\vec{z}_2, \vec{H}) = 70°32'$, 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 Θ of the isomorphous compound $ZnCr_2O_4$. Our result throws doubt on the positive J value found by Blazey[14] from the fluorescence spectrum of Cr-doped $ZnAl_2O_4$ powders.

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

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

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

$$j = -\tfrac{1}{2}(\rho^2/c\,r_0)\quad , \tag{6}$$

where $\rho = dJ/dr_0$ and c is the elastic stiffness. Motida and Miyahara[20] recently pointed out that ρ is rather large for 90° Cr-Cr interactions as a consequence of a subtle balance between negative direct[21] (Cr-Cr) exchange and positive indirect (Cr-O-Cr) exchange interactions. A plot[20] of Θ vs r_0 for the oxides $LiCrO_2$, $ZnCr_2O_4$, $MgCr_2O_4$, $NaCrO_2$, $HCrO_2$, $DCrO_2$, $CuCrO_2$, and $CdCr_2O_4$ gives $d\Theta/dr_0 = 35\times10^{10}\ ^\circ\mathrm{K/cm}$, which leads to $\rho = 64\times10^{-7}$ erg/cm if the assumption is made that Θ is mainly determined by nn interactions. With $c \simeq 20\times10^{11}\ \mathrm{dyn/cm^2}$ and $r_0 = 2.94\times10^{-8}$ cm we finally obtain $j/k = -2.5\ ^\circ\mathrm{K}$, in excellent agreement with experiment.

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