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Nuclear Magnetic Resonance of Cd in $CdCr_2Se_4$ and $CdCr_2S_4$, and Transferred Spin Polarization in Chromium Chalcogenide Spinels

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Purely isotropic hyperfine fields have been observed for ^{111}Cd and ^{113}Cd by zero-field NMR in both ferromagnetic $CdCr_2Se_4$ and $CdCr_2S_4$. The values at 4.2 K are $+136.2\pm0.2$ and $(+)\ 167.0\pm0.2$ kOe, respectively. Combined with earlier results for ^{53}Cr and ^{77}Se in $CdCr_2Se_4$, this work allows estimates to be made of the amount of unpaired spin covalently transferred to the nonmagnetic ions. Transfers between ligands and the 4*s* level of Cr^{3+} are particularly important. Some consequences for the magnetic properties of the system are discussed.

INTRODUCTION

THE group of compounds of normal cubic spinel structure, with magnetic ions (Cr^{3+}) only in *B* sites, and with chalcogen (S or Se) ion ligands, is a relatively new class of magnetic materials.[1,2] We have previously reported[3] zero-field nuclear magnetic resonance (NMR) results for the hyperfine fields at ^{53}Cr and ^{77}Se in the ferromagnetic state of $CdCr_2Se_4$. Other work on related compounds show very similar results.[4,5] We have now extended these measurements to ^{111}Cd and ^{113}Cd in both $CdCr_2Se_4$ and $CdCr_2S_4$.

The material $CdCr_2Se_4$ is of particular interest because all of the constituent nuclei have thus been examined by NMR. It is fairly representative of this class of spinels. The resonance features of particular interest are the low value of the hyperfine field at the ^{53}Cr nucleus and large values at the other nuclei in the system, as compared with fields in magnetic compounds with oxygen or fluorine ligands. These results are indicative of sizable covalent transfers of electronic spin polarization. With the field values obtained, we shall evaluate some of the relevant spin transfer coefficients, which in turn can help to explain the magnetic properties of the system.

EXPERIMENT

A portion of the spinel lattice is illustrated in Fig. 1. The lattice has symmetry $Fd3m$ (O_h^7). In the present system, Cr ions are located in *B* sites $(\bar{3}m)$, Cd or other nonmagnetic metal ions are in *A* sites $(\bar{4}3m)$, and the ligands lie in sites with point symmetry $3m$. In all of the materials to be discussed, the ligand position parameter u has the value[1] 0.390 instead of the value $\frac{3}{8}$ which would yield the ideal spinel form. In the ideal case, an *A* site is surrounded by a regular tetrahedron of ligands, a *B* site by a regular octahedron. The change to the proper value of u merely enlarges the tetrahedron radially by 12%, but it introduces a trigonal distortion of the octahedron along a cube diagonal, causing the line from the *B* site to ligand to be rotated 5°10′ toward the distortion axis and to be shortened by 6%. Each ligand connects one *A* site to three *B* sites.

Our previous zero-field NMR results[3] obtained at 4.2 K are summarized in Table I, together with the results of Berger *et al.* for isomorphous ferromagnetic $CdCr_2S_4$ and $HgCr_2Se_4$,[4] and for metamagnetic $HgCr_2S_4$.[5] Their results[4] for $CdCr_2Se_4$ are in excellent agreement with those shown. In each of these materials, the resonance frequency of ^{53}Cr depends on the direction of magnetization and can be written

$$\nu_{m\rightarrow m-1}=\left|(\gamma/2\pi)H_{\rm iso}+\left((\gamma/2\pi)H_{\rm ax}+\tfrac{1}{2}\nu_Q(m-\tfrac{1}{2})\right)(3\cos^2\theta-1)\right|.$$

Here $H_{\rm iso}$ represents the isotropic and $H_{\rm ax}$ the constant coefficient of the axially symmetric (angularly-dependent) hyperfine field. The quadrupolar contribution is expressed with the usual coefficient ν_Q. The angle θ is measured between the direction of magnetization and the threefold (cube diagonal) symmetry axis of the Cr site. The same expression, without the quadrupolar contribution, also describes the ^{77}Se results.

Using marginal and superregenerative oscillators and also the spin-echo technique, we have now observed the zero-field nuclear resonances of ^{111}Cd and ^{113}Cd at 4.2 K in the same powdered sample of $CdCr_2Se_4$ and in $CdCr_2S_4$. Only isotropic hyperfine fields are observed,

TABLE I. 4.2 K zero-field resonance data.

	Cr (*B* site)			Ligand		*A* site[a]
	$H_{\rm iso}$ (kOe)	$H_{\rm ax}$ (kOe)	$\frac{1}{2}\nu_Q$ (MHz)	$H_{\rm iso}$ (kOe)	$H_{\rm ax}$ (kOe)	$H_{\rm iso}$ (kOe)
$CdCr_2Se_4$[b,c]	−182.5	+2.30	0.90	−98.0	+9.2	+136.2 ±0.2
$CdCr_2S_4$[c]	−191.0	+2.07	0.95			(+)167.0 ±0.2
$HgCr_2Se_4$[c]	−178.3	+2.3	0.98	−91	+9.75	
$HgCr_2S_4$[d]	−190	+2.3	0.95			

[a] Present work.
[b] G. H. Stauss, M. Rubinstein, J. Feinleib, K. Dwight, N. Menyuk, and A. Wold, J. Appl. Phys. **39**, 667 (1968).
[c] S. B. Berger, J. I. Budnick, and T. J. Burch, J. Appl. Phys. **39**, 658 (1968).
[d] S. B. Berger, T. J. Burch, and J. I. Budnick, Bull. Am. Phys. Soc. **13**, 492 (1968).

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[1] P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin, Phys. Rev. **151**, 367 (1966).
[2] N. Menyuk, K. Dwight, R. J. Arnott, and A. Wold, J. Appl. Phys. **37**, 1387 (1966).
[3] G. H. Stauss, M. Rubinstein, J. Feinleib, K. Dwight, N. Menyuk, and A. Wold, J. Appl. Phys. **39**, 667 (1968).
[4] S. B. Berger, J. I. Budnick, and T. J. Burch, J. Appl. Phys. **39**, 658 (1968).
[5] S. B. Berger, T. J. Burch, and J. I. Budnick, Bull. Am. Phys. Soc. **13**, 472 (1968).

with the values shown in Table I. A single line with a width of about 200 kHz, and with no structure, was observed from each isotope in the sulfide; the proper spacing of the lines identified their origins. In the selenide, additional signals could be distinguished about 100 kHz below the main peaks in frequency, and they were characterized by shorter relaxation times and by echoes of significantly shorter time duration (presumably from nuclei within domain walls). The shift corresponds to a field of about 100 Oe, which is comparable to the magnitude of the bulk anisotropy field observed for $CdCr_2Se_4$.[6]

Application of an external field to $CdCr_2Se_4$ causes the Cd frequencies to increase, demonstrating that the hyperfine field is positive (with respect to the magnetization direction); this is presumed to be the case in the sulfide also. The slope of frequency versus field confirms the identification of the resonances. Changing the temperature of $CdCr_2Se_4$ to 77 K reduces the Cd hyperfine field to 107.1±0.2 kOe, in good agreement with the value 107.4±0.2 predicted by scaling the 4.2 K result in proportion to sample magnetization (or, equivalently,[3] to the Cr or Se field).

DISCUSSION

Henning[7] has described the semiquantitative linear relationship which exists between isotropic hyperfine field strength at the magnetic ion nucleus and covalency [defined, in terms of differences in electronegativity (following Pauling) between the magnetic ion and neighboring ligands]. Such a relationship appears to hold for Cr^{3+}-containing compounds, including the ones discussed here, with an extrapolated value of -450 kOe for zero covalency (isolated ion). There is a significant reduction in magnitude of the Cr^{3+} hyperfine field when the ion is bound into a crystal, attributed by Henning mainly to transfer of polarized ligand electrons into higher s orbital states of the magnetic ion via excited molecular orbitals. However, the formation of the ground-state molecular orbitals can alone produce this effect and will be the only process considered here. The resultant transfer of ligand electrons and delocalization of Cr electronic polarization affect also the axial and quadrupolar parts of the Cr nuclear signal; more significantly for our purposes, they lead to the hyperfine fields at surrounding ions as well.

Within an ionic model, direct dipolar interactions with the magnetic ions ($S=\frac{3}{2}$) in the ideal spinel ($u=\frac{3}{8}$) result by symmetry in zero field at A sites or ligands,[8] and give $H_{\mathrm{ax}}=+1300$ Oe at Cr sites. Changing the u to 0.390 does not alter the value at the Cr or Cd sites but it introduces an H_{ax} at Se of about 500 Oe from nearest neighbors. The computed[9] electrostatic field gradient at Cr in the ideal ionic model seems to be a factor of 2 less than observed—increasing u to 0.390 causes a reduction almost to zero. To explain the experimental results, including the remaining H_{ax} of about 1 kOe at Cr, it is thus necessary to assume that spin polarization is transferred between the Cr ions and the ligand and A sites. The basic premise in what follows is that the effects of overlap and charge transfer which combine to produce the transfer of spin polarization are small perturbations to the ionic model and the effects of individual bonds are independent and additive. We shall leave aside the question of the quadrupole interaction, which can be modified by any rearrangement of charges.

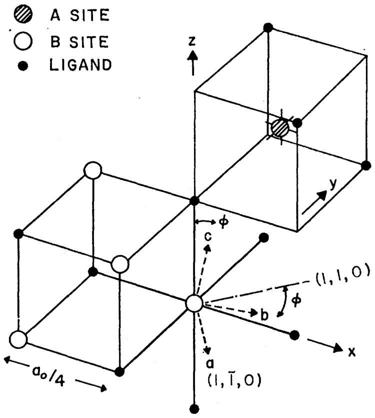

FIG. 1. A portion of the spinel lattice, with coordinates used in discussion.

Molecular Orbitals

Following Watson and Freeman,[10] we describe the spin transfer in a single bond in terms of molecular orbitals. For a specific spin orientation, if a ligand orbit x and metal orbit y are both occupied, they will form bonding and antibonding molecular orbitals,

$$N_B(x+By) \quad\text{and}\quad N_A(y-Ax),$$

where $N_B^{-2}=(1+B^2+2BS)$, $N_A^{-2}=(1+A^2-2AS)$, and the overlap $S=\langle x|y\rangle$. Orthogonality of these orbitals requires that $A=B+S$. To lowest order, the electronic occupation of the ligand orbit is thus $N_B^2+A^2N_A^2=1+S^2$ and at the metal ion it is $N_A^2+B^2N_B^2=1+S^2$ also, for this one spin orientation. If the opposite spin state is equivalently populated, the same occupations result and the net spin at both ions vanishes, even if B changes with spin direction, as might occur in connection with

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[6] R. C. LeCraw, H. von Philipsborn, and M. D. Sturge, J. Appl. Phys. 38, 965 (1967).

[7] J. C. M. Henning, Phys. Letters 24A, 40 (1967).

[8] B sites and ligands form a NaCl-type structure with half the B sites empty, the empty sites being related by inversion through the ligands to occupied sites. If occupied, the empty sites would contribute equally with the occupied B sites, but in the NaCl structure the dipolar field at the ligand will be zero.

[9] This was done using the solution of R. A. Johnson and D. W. Healy, Jr., J. Chem. Phys. 26, 1031 (1957), modified by removal of Lorentz-field terms.

[10] R. E. Watson and A. J. Freeman, Phys. Rev. 134, A1526 (1964).

Hund's rule. In the present problem, we have rather the situation that the important metal orbits are empty for one or both spin orientations. To the same order of approximation, with an empty metal orbit, in the ground state only the bonding orbital is formed, with resultant occupation N_B^2 at the ligand and $B^2N_B^2$ at the metal ion. With the metal orbits empty for both spin states, the net unpaired spin at the ligand is thus given by

$$f=N_{B\uparrow}^2-N_{B\downarrow}^2\approx(B\downarrow-B\uparrow)(B\uparrow+B\downarrow+2S)\,, \qquad (1)$$

and at the metal ion we have

$$g=B\uparrow^2-B\downarrow^2=(B\uparrow-B\downarrow)(B\uparrow+B\downarrow)\,; \qquad (2)$$

these values depend essentially on the difference between the $B\uparrow$ and $B\downarrow$ coefficients. If excitation into the antibonding orbital occurs, it can be largely allowed for by a change in the effective value of B. For a half-filled metal orbit with spin up only, the unpaired ligand spin becomes

$$f=(1+S^2)-N_{B\downarrow}^2=(B\downarrow+S)^2\,; \qquad (3)$$

at the metal ion the corresponding unpaired spin is

$$g=(1+S^2)-B\downarrow^2N_{B\downarrow}^2\approx1-(B\downarrow+S)^2+2S(B\downarrow+S) \qquad (4)$$
$$=1-f+2Sf^{\frac{1}{2}}.$$

The $3d$ electronic levels of the magnetic ion in an ideal octahedral complex split, in the strong crystal field approximation, into a lower degenerate t_{2g} triplet and a higher e_g doublet. The three electrons of the $3d^3$ configuration for Cr^{3+} are placed in the t_{2g} levels with parallel spin polarization by Hund's rule. Coupled to this ion in the complex are six ligand ions of $4s^24p^6(Se^{2-})$ or $3s^23p^6(S^{2-})$ configuration. Thus, if a ligand-Cr bond is in the z direction of the cubic crystal lattice, σ molecular orbitals with axes in the direction of the bond will mix empty $d(z^2)(e_g)$ or $4s$ orbits of Cr^{3+} with the outer occupied ligand s or p_z orbits, while π orbitals with axes normal to the bond direction will connect ligand p_x and p_y orbits with occupied and empty t_{2g} orbits of Cr^{3+}. Molecular orbitals with inner ionic levels, particularly $3d$ of Se, are ignored since the overlaps are small and these levels are considerably lower in energy.

Determination of Unpaired Spin Transferred

In the σ orbitals, because of exchange interactions, it is energetically favorable for small amounts of unpaired spin to go into the Cr e_g and $4s$ orbitals, preferentially polarized parallel to the existing Cr spin polarization.[11] At the ligand, the effect of this is to leave net amounts f_σ and f_s of unpaired electronic spin negatively polarized in p_z and $4s$ orbits. In the π orbitals only ligand electrons spin polarized negatively can be transferred into the empty t_{2g} orbits, leaving amounts f_π of positive spin polarization in the ligand p_x and p_y orbits. Polarization of the p orbits will result in some core polarization of inner s electrons at the ligand, effectively modifying f_s.

In the ideal case, $u=\frac{3}{8}$, the ligand ion is located at the corner of a cube connected to three Cr ions lying on adjacent corners (Fig. 1). Combining the contributions of only these three nearest-neighbor Cr ions to the hyperfine interaction at the ligand nucleus yields a purely isotropic field. At Cr sites, a similar cancellation occurs of anisotropic field components produced by the octahedron of nearest-neighbor ligands. Introduction of a trigonal distortion through an increase in the value of u forces the ligand toward the plane of its three neighbor Cr's. One then anticipates some modification of f_s due to the change in bond length. In addition, the density of transferred spin polarization in the ligand p orbits will become anisotropic (axially symmetric). This corresponds to breaking the original threefold degeneracy of the p electrons into a singlet and a doublet. At the Cr sites, the effect will be similar, but since the distortion as seen by a Cr ion represents a movement of ligands away from the equatorial region of the trigonal axis of the Cr, the anisotropy in polarization density, which occurs in t_{2g} orbits and corresponds again to breaking the degeneracy, will be in the opposite sense from that at the ligand. However, since the transferred polarizations at the two sites are of opposite signs themselves, the actual signs of H_{ax} at both should be the same, as is observed.

We note that the Cr-ligand bond axis which is now near but no longer exactly in the z direction, lies in a mirror plane containing the nearest A site to the ligand, so that the tensor describing the transferred hyperfine interaction between one Cr ion and adjacent ligand nucleus has a principal direction, labeled a, normal to that plane (Fig. 1). Setting this direction as $(1,\bar{1},0)$, the directions of the principal axes b and c (nearest to the z direction) become $(\frac{1}{2}\sqrt{2}\cos\varphi,\frac{1}{2}\sqrt{2}\cos\varphi,-\sin\varphi)$ and $(\frac{1}{2}\sqrt{2}\sin\varphi,\frac{1}{2}\sqrt{2}\sin\varphi,\cos\varphi)$ in terms of the angle φ between the c and z directions. In the principal coordinate system, the hyperfine interaction becomes $A_aI_aS_a+A_bI_bS_b+A_cI_cS_c$. Keeping the ligand nuclear spin I and all the Cr spins S fixed in direction and transforming the interaction appropriately to the three Cr neighbors of the ligand, one obtains a total ligand hyperfine interaction

$$\begin{aligned}(A_a+A_b+A_c)\mathbf{I}\cdot\mathbf{S}+\tfrac{1}{2}(-A_a+A_b\cos^2\varphi+A_c\sin^2\varphi\\ +2\sqrt{2}(A_c-A_b)\cos\varphi\sin\varphi)\\ \times(I_x(S_y+S_z)+I_y(S_x+S_z)+I_z(S_x+S_y)).\end{aligned}$$

The isotropic field is dominant; keeping of the rest only the part parallel to $\mathbf{S}$ yields the effective interaction

$$\begin{aligned}\mathbf{I}\cdot\mathbf{S}[(A_a+A_b+A_c)+\tfrac{1}{2}(-A_a+A_b\cos^2\varphi+A_c\sin^2\varphi\\ +2\sqrt{2}(A_c-A_b)\cos\varphi\sin\varphi)(3\cos^2\theta-1)],\end{aligned}$$

where θ is the angle between $\mathbf{S}$ and the ligand trigonal axis.

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[11] Cf., D. E. Rimmer, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and the Physical Society, London, 1965), p. 337.

Following Abragam,[12] and neglecting the small direct dipolar contribution, the A's can be written for a single bond

$$A_a=(1/2S)[f_sA_s+(2f_a-f_b-f_c)A_p],$$
$$A_b=(1/2S)[f_sA_s+(-f_a+2f_b-f_c)A_p],$$
$$A_c=(1/2S)[f_sA_s+(-f_a-f_b+2f_c)A_p],$$

so that the interaction becomes

$$(\mathbf{I}\cdot\mathbf{S}/2S)\{3f_sA_s+\tfrac{3}{2}A_p(3\cos^2\theta-1)[-f_a+f_b(\cos^2\varphi -2\sqrt{2}\cos\varphi\sin\varphi)+f_c(\sin^2\varphi+2\sqrt{2}\cos\varphi\sin\varphi)]\}.$$

Here $A_s=(16\pi/3)g_n\beta_n\beta_e|\psi_s^2(0)|$ and $A_p=\frac{4}{5}g_n\beta_n\beta_e\langle r^{-3}\rangle_p$ evaluated at the ligand. The f's in the braces represent the unpaired spin in ligand p orbits with axes a, b, and c. From this result we obtain the isotropic hyperfine field

$$H_{\text{iso}}(\text{Se})\approx(1/g_n\beta_n)(3A_s/2S)f_sS =3f_s(8\pi/3)\beta_e|\psi_s^2(0)|. \quad (5)$$

The observed sign is negative, in agreement with the expectation that f_s is negative.

For the special case $\cos\varphi=1$ with c along the bond direction, $f_c=f_\sigma$, and $f_a=f_b=f_\pi$, the axial part disappears. Going to the proper structure considerably complicates the situation; σ bonds may then include some mixing between ligand p and the Cr t_{2g} orbits, and there can also be some overlap between the ligand s and the t_{2g}'s. In addition, there is mixing of σ and π in f_b and f_c when c is not the bond direction.

Two simple cases can be considered, assuming that the above complications are small: (a) Taking $\cos\varphi\approx1$, $f_c\approx f_\sigma$, $f_a\approx f_{\pi a}$, and $f_b\approx f_{\pi b}$, we obtain the axial hyperfine field

$$H_{\text{ax}}(\text{Se})\approx(1/g_n\beta_n)\tfrac{3}{2}(A_p/2S)(f_{\pi b}-f_{\pi a})S =\tfrac{3}{5}\beta_e(f_{\pi b}-f_{\pi a})\langle r^{-3}\rangle_p; \quad (6a)$$

the sign is as observed if $f_{\pi b}$ exceeds $f_{\pi a}$ and both are positive as anticipated earlier. (b) Alternatively, if the c direction is along the bond, for $u=0.390$ the angle $\varphi=-5°10'$. Then, the resultant axial-field value becomes

$$H_{\text{ax}}(\text{Se})\approx\tfrac{3}{5}\beta_e(1.25f_{\pi b}-f_{\pi a}-0.25f_\sigma)\langle r^{-3}\rangle_p. \quad (6b)$$

The sign of H_{ax} agrees with observation if the term in parentheses is positive. In this case, especially for appreciable f_σ, it is not necessary for $f_{\pi b}$ to be much different from $f_{\pi a}$ to achieve a significant asymmetry. The two cases discussed should form limits to the proper configuration. To encompass both, we can write

$$H_{\text{ax}}(\text{Se})\approx\tfrac{3}{5}\beta_e\Delta f\langle r^{-3}\rangle_p. \quad (7)$$

A similar solution describes the effect of the u distortion of the ligand octahedron on the hyperfine field at Cr. With the same orientation of a, b, and c axes, the same tensor form describes the effect of a single bond at Cr. The hyperfine interaction is found to be exactly that for the ligand, if A_a, A_b, and A_c are replaced by $2A_a'$, $2A_b'$, and $2A_c'$ and if further the angle φ is changed to $-\varphi$. The A' are related to the amounts of unpaired spin g in a manner similar to that relating the A and f. The isotropic contribution to Cr, by which the pure ionic field of about -450 kOe is reduced to the observed value, is given by

$$H_{\text{iso}}(\text{Cr})=6g_s(8\pi/3)\beta_e|\psi_{4s}^2(0)|. \quad (8)$$

If one limits consideration to orbitals with t_{2g} Cr components, the anisotropic parts of A' become

$$2A_a'=2(A_d/2S)(2g_a-g_b-g_c),$$
$$2A_b'=2(A_d/2S)(-g_a+2g_b-g_c),$$
$$2A_c'=2(A_d/2S)(-g_a-g_b+2g_c),$$

where $A_d=-(4/7)g_n\beta_n\beta_e\langle r^{-3}\rangle_d$ evaluated at Cr. Corresponding to the two simple cases (a) and (b) for the ligand, at the Cr site

$$H_{\text{ax}}(\text{Cr})\approx(6/7)\beta_e(g_{\pi a}-g_{\pi b})\langle r^{-3}\rangle_d \quad (9a)$$

or

$$H_{\text{ax}}(\text{Cr})=(6/7)\beta_e(g_{\pi a}-0.74g_{\pi b}-0.26_c)\langle r^{-3}\rangle_d. \quad (9b)$$

Corresponding to Eq. (7), we can write

$$H_{\text{ax}}(\text{Cr})\approx(6/7)\beta_e\Delta g\langle r^{-3}\rangle_d. \quad (10)$$

To relate the Cr and Se results, we note that the geometrical arrangement of symmetry axes for a t_{2g} orbit and the overlapping ligand p orbit is such that g_a corresponds to f_b and g_b to f_a; g_c can be taken as unity. Inclusions of the $d(z^2)(e_g)$ orbit of Cr with unpaired spin g_σ modifies g_c to $1-g_\sigma$. Thus from Eqs. (4) and (8) we can write for the two special cases

$$H_{\text{ax}}(\text{Cr})=(6/7)\beta_e\langle r^{-3}\rangle_d(-f_{\pi b}+f_{\pi a} +2S_bf_{\pi b}^{1/2}-2S_af_{\pi a}^{1/2}), \quad (11a)$$

or

$$H_{\text{ax}}(\text{Cr})=(6/7)\beta_e\langle r^{-3}\rangle_d(-f_{\pi b}+0.74f_{\pi a} +2S_bf_{\pi b}^{1/2}-1.48S_af_{\pi a}^{1/2}+0.26g_\sigma), \quad (11b)$$

where $S_b=\langle d_a|p_b\rangle$, $S_a=\langle d_b|p_a\rangle$. Thus, after removing the ionic dipolar contributions, comparing Eqs. (6) with Eqs. (11), it appears that the dissimilar magnitudes of H_{ax} at Se (8.7 kOe) and Cr (1 kOe), and their similar signs, result from near equality between the overlap S and charge transfer contribution $B\downarrow$ to the unpaired spin fraction f in Eq. (3), and/or from the effects of f_σ and g_σ brought about by the trigonal distortion.

The quantities g_s and f_s are not simply related to each other, since g_s contains components transferred by σ orbitals from both the ligand $4p$ and $4s$ levels; f_s similarly involves spin transferred from the ligand $4s$ to both Cr e_g and $4s$ orbitals. The information contained in the incompletely known quantities f_σ and g_σ would be necessary to separate these various contributions, using Eqs. (1) and (2).

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[12] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), p. 191.

TABLE II. Fractional unpaired spin transfers in $CdCr_2Se_4$.

Site	Transfer fraction	Wave function used (a.u.) (1 a.u. $=6.77\times10^{24}$ cm^{-3})
Se	$f_{4s}=-(4.0\text{–}4.4)\times10^{-3}$	$\psi_{4s}^2(0)=14\text{–}15.5$
	$\Delta f_{4p}=2.9\text{–}3.3\times10^{-2}$	$\langle r^{-3}\rangle_{4p}=7\text{–}8$
Cd	$f_{5s}\approx2.2\times10^{-3}$ (1.8×10^{-3} in $CdCr_2S_4$)	$\psi_{5s}^2(0)\approx12$
Cr	$\Delta g_{3d}\approx4.6\times10^{-3}$	$\langle r^{-3}\rangle_{3d}=3.96$
	$g_{4s}\sim2.8\times10^{-2}$	$\psi_{4s}^2(0)$ est. ~3

At the Cd site, symmetry forces the anisotropic part of the transferred hyperfine interaction to cancel, leaving only an s-electron term. Denoting by f_s the unpaired spin transferred to a Cd by one Cr, we find that the 12 equivalent nearest Cr's, coupled via four ligands, produce at Cd

$$H_{\text{iso}}(\text{Cd})=12f_s(8\pi/3)\beta_e|\psi_s^2(0)|\,, \tag{12}$$

with the sign given by the sign of the polarization of the f_s. This is observed to be positive. Since the Cd^{2+} ion configuration is $5s^0$, the results suggest that electrons are transferred into the 5_s orbit with positive polarization by indirect transfer[13] from the Cr or by mixing of s and p orbits in the ligand-Cd σ bond under conditions that the p's possess a net positive polarization at the ligand. Core polarization of inner Cd s electrons might result from polarized Cd p electrons.[14,15] However, reasonable values for p polarization yield core contributions much smaller than the observed isotropic fields, so this contribution will be neglected.

Making use of the results obtained above in Eqs. (5), (7), (8), (10), and (12), we can evaluate the amounts of unpaired spin transferred to the various sites. These are shown in Table II as the amount per Cr neighbor, or per Cr-ligand bond in the case of Cr. The wave-function values used represent estimates of the effect of ionization to something between Se^- and Se^{2-} on the free-ion values of neutral Se,[16] $\psi_{4s}^2(0)=15.8$, $\langle r^{-3}\rangle_{4p}=9.46$; interpolation to Cd^+-Cd^{2+} from the values[17,18] for neutral Ag, $\psi_{5s}^2(0)=0.9$, and Sb^{3+}, $\psi_{5s}^2(0)=19.2$; and the published value[19] of $\langle r^{-3}\rangle_{3d}$ for Cr^{3+}. The value of $\psi_{4s}^2(0)$ for Cr^{3+} is a crude estimate. Presumably, mainly for reasons of low natural abundance, the resonance of ^{31}S was not observed. One anticipates values of f no greater than for Se; on the other hand, the wave-function results of Czyzak[20] for S^{2-} and S^- give $\psi_{3s}^2(0)=7$ and $\langle r^{-3}\rangle_{3p}=3.7$, which would imply very much reduced hyperfine-field values.

With the information available it is not possible unambiguously to separate further the various overlap and charge transfer coefficients. One particular model, however, is suggestive of orders of magnitude. Assuming that the c axis lies along the bond direction, case b, and arbitrarily taking $f_{\pi a}=f_{\pi b}=-f_\sigma$ in Eq. (6b), the value of Δf leads to $f_\sigma=-0.06$. Then, from the value of Δg, using Eqs. (3) and (11b), with the further assumption that $S_a=S_b\approx B_a$ one then obtains $S_a=0.12$, $g_\sigma=0.02$. Furthermore, from the large size of f_σ and g_s with respect to f_s, one would expect that the major part of these larger terms is contributed by a $4p_\sigma(\text{Se})-4s(\text{Cr})$ orbital.

Within the set of materials discussed, the principal pattern of variation with covalency is as follows: For fixed A-site occupancy, increasing the B-ligand covalency decreases the magnitudes of the isotropic fields at both A and B sites. For fixed ligand type, an increase in A-ligand covalency results in a decrease in the magnitude of the isotropic field at the ligand site and a smaller decrease at the B site. The axial fields (largely determined by ionic contributions at the Cr site) are less sensitive.

These effects are explicable if one assumes that increasing covalency aids transfer of ligand s and particularly p_σ electrons into empty metal s orbits. This is consistent with the decrease in energy required for such transfer. As described earlier, spin transferred into B site s orbits produces a positive field there opposing the core polarization field. At the ligand this results in negative polarization of the s and p_σ orbits, which thus produce a negative isotropic field, and in conjunction with the trigonal lattice distortion, a positive contribution to the axial field. The sense of the A-site polarization corresponds to the net positive polarization of the ligand p orbits. Changing the ligand type to increase covalency will decrease the amount of positive s polarization on the A site, first, by transferring to the A site more of the negative ligand s polarization and, second, by augmenting the negative ligand p_σ contribution, thus reducing the net ligand p polarization. Changing only the A-site occupant to increase covalency will similarly cause transfer of some of the electronic polarization of the ligand to the A site, reducing the isotropic field at the ligand; this transfer, slightly repopulating the spin-up ligand s level, will lead to a small additional transfer to the B site.

Influence on Magnetization

It is interesting to consider the magnetization properties in connection with these results. The Cr chalco-

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genide spinels have been shown[1,21] to order through the effect of nearest-neighbor ferromagnetic superexchange in competition with mainly antiferromagnetic secondary couplings, roughly 0.01–0.1 times as strong, to something like 30 more distant neighbors. We conclude that the great range of temperature over which a $T^{3/2}$-only dependence exists[3] for the magnetization of $CdCr_2Se_4$ is mainly the result of a cancellation among the many exchange contributions to the next two higher-order terms in the spin-wave expansion.

When the secondary couplings taken as a group are strong and negative, they will tend to stabilize antiferromagnetic or spiral configurations (e.g., $HgCr_2S_4$ [5] or $ZnCr_2Se_4$ [21]). If they are sufficiently weak, however, it is possible for ferromagnetic ordering to occur. In accordance with Anderson's model of superexchange,[22,14] there is a direct relationship between the product of transferred spin densities f in the various ligand orbits involved in a superexchange linkage path, and the strength of the superexchange interaction. The net exchange will be the sum of the contributions from all the linkages connecting two magnetic ions. The nearest-neighbor exchange in the present case involves 90° bonds through common ligands, while the secondary linkages involve two ligands overlapping directly or mixed on intermediate (mainly A) cation sites to which they are covalently bonded.

In the previous discussion we developed the picture of large transfer fractions f, with positive polarization in the f_π parts and negative polarization of the f_σ. The sign of each linkage's contribution to exchange will thus depend on whether a σ orbital is included once or an even (zero or two) number of times. Furthermore, in the overlap of two ligands, the interaction can be modified greatly by the intervention of a cation intermediary.

From the magnetic information available[1] for the materials under discussion, it is found that the nearest-neighbor ferromagnetic exchange increases and the net antiferromagnetic strength of the secondary exchanges decreases somewhat in magnitude as the ligand is changed from S to more covalent Se, so that the ferromagnetic critical temperature and paramagnetic Curie temperature both rise. Changing the A-site occupant from Cd to more covalent Hg, however, while still causing some increase in nearest-neighbor exchange, makes the secondary exchanges considerably more strongly antiferromagnetic to the extent that the critical temperatures are both reduced. To explain these effects, we note that the net nearest-neighbor exchange is strengthened[14] by the increases in absolute magnitude of both f_π and f_σ which occur with increasing Cr-ligand covalency.

For the other exchange couplings, there exists a complicated balance between the strength of linkages with even and odd contributions from f_σ terms. One can only speculate on how this is altered by covalency. The balance changes a little to reduce the net antiferromagnetism when S is replaced by Se and f_σ becomes relatively stronger. It is observed that the secondary linkages become more antiferromagnetic when Cd is replaced by Hg, even though they are relatively weaker in both cases than for the less covalent Zn in $ZnCr_2Se_4$.[21] This implies that linkages susceptible to modification by the A-site intermediaries are, in sum, fairly strongly antiferromagnetic when this modification is slight, as for Zn, but that increasing A-site covalency quenches direct ligand-ligand overlap. Thus, the linkages for Cd or Hg depend upon the overlap taking place at the A site. These modified paths taken together are less antiferromagnetic than before, but become individually stronger with increasing A-site covalency.

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