

On inserting the special form (38) for W , we have

$$\frac{1}{\tau} = \alpha \sum_{ij} \left(\frac{1}{Z_a} + \frac{1}{Z_b} \right) u(ia; jb) \times \frac{E(i,a) - E(j,b)}{\exp[E(i,a)/kT] - \exp[E(j,b)/kT]}.$$

When $E(i,m) \ll kT$, we have $Z_a \approx Z_b \approx \eta$, the number of

levels in each group and the right-hand factor $\rightarrow 1$, giving

$$\frac{1}{\tau} = -\frac{2}{\eta} \alpha kT \sum_{ij} u(ia; jb). \quad (E3)$$

Since the groups are in thermal equilibrium, the magnetization for a given distortion is linearly related (independent of time) to N_a , so that the magnetization of each distortion has the same relaxation given by (E3).

Systematics of the Hyperfine and Exchange Interactions in the Chromium Chalcogenide Spinel

S. B. BERGER*

RCA Laboratories, Princeton, New Jersey 08540

AND

J. I. BUDNICK AND T. J. BURCH

Fordham University,† Bronx, New York 10458

(Received 10 June 1968)

The NMR of nuclei at each site in the cadmium and mercury chromium chalcogenide spinels has been studied at 1.4°K. Experimentally, we find an approximately linear relation between the isotropic hyperfine field of ^{53}Cr nuclei and the near-neighbor chromium-chromium exchange constants. This observation is interpreted in terms of a systematic variation in covalency and constant overlap for these compounds. The ^{77}Se isotropic hyperfine field is large and oppositely directed to the magnetization. This field can be understood in terms of a spin polarization of Se s orbitals by the unpaired Cr spins. The Cr and Se results are consistent with a theoretical formulation due to Huang and Orbach. The ^{199}Hg , ^{201}Hg , ^{111}Cd , and ^{113}Cd hyperfine fields are found to be isotropic, large, and positive with respect to the magnetization. These fields are shown to be mainly due to overlap of unfilled outer s shells of these nonmagnetic ions with the Cr $3d$ orbits.

THE magnetic chromium chalcogenide spinels offer an unique opportunity to study the hyperfine interactions of nuclei in a system for which the relevant exchange interactions have been independently determined.¹ We have investigated the NMR of all nuclei except sulfur in CdCr_2S_4 , CdCr_2Se_4 , HgCr_2S_4 , and HgCr_2Se_4 . The similar angular relationship of the cations to the anions in these compounds is reflected by their identical crystallographic u parameters.¹ This factor, the essentially constant ionic radii,¹ and the direct correlation of our NMR data to the nearest-neighbor (nn) exchange parameter allow reliable conclusions concerning covalency and overlap to be drawn for this system.²

In this paper we report new NMR data for these compounds from which we conclude: (1) the ^{53}Cr isotropic hyperfine interaction exhibits an approxi-

mately linear variation with the nn exchange interaction, and (2) the nonmagnetic cation (Cd or Hg) hyperfine interaction and the next nearest-neighbor (nnn) chromium exchange interaction¹ are dominated by an overlap contribution, since both are noted to decrease with increasing lattice parameter. The first observation differs from that found for the dissimilar manganese monochalcogenide series³ and is describable as a systematic variation of the covalency in the present compounds consistent with a theoretical evaluation of the important nn exchange paths.⁴ This covalency change is also a critical part of our interpretation of the Se hyperfine interactions.

In Table I, a summary of our results for the isotropic hyperfine fields $H_{i,so}$ in these compounds is presented. The data were obtained at 1.4°K using spin-echo techniques on polycrystalline samples. For the noncubic sites the spectra were analyzed to determine the isotropic contribution.^{5,6} The signs were found by measuring the frequency shift upon application of a magnetic

* Jointly sponsored by Air Force Cambridge Research Laboratories, Office of Aerospace Research, under Contract F19628-67-CO175, and RCA Laboratories, Princeton, New Jersey, but this report does not necessarily reflect endorsement by the sponsor.

† Supported in part by the National Science Foundation.

¹ P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin, *Phys. Rev.* **151**, 367 (1966).

² R. E. Watson and A. J. Freeman, in *Hyperfine Interactions* edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967), pp. 81–91.

³ E. D. Jones, *Phys. Rev.* **151**, 315 (1966).

⁴ Nai L. Huang and R. Orbach, *J. Appl. Phys.* **39**, 426 (1968).

⁵ S. B. Berger, J. I. Budnick, and T. J. Burch, *J. Appl. Phys.* **39**, 658 (1968).

⁶ G. H. Stauss, M. Rubinstein, J. Feinleib, K. Dwight, N. Menyuk, and A. Wold, *J. Appl. Phys.* **39**, 667 (1968).

field and are relative to the magnetization direction. The NMR lines of Hg nuclei in HgCr_2S_4 were very anisotropic in contrast to the results for the nonmagnetic cations in the other compounds.⁷ Table I also contains the nn and nnn exchange parameters J and K , respectively, taken from the literature.¹

In Fig. 1, H_{iso} for ^{53}Cr is plotted as a function of J . An approximately linear dependence is observed which can be explained through consideration of the mechanisms which give rise to H_{iso} and J . Huang and Orbach have treated the nn exchange theoretically.⁴ They find, neglecting direct exchange, a linear dependence of J on covalency. They expect that the additive overlap contributions to the superexchange will be constant for these compounds. On the other hand, H_{iso} is known to decrease linearly with increasing covalency^{2,8} but to increase with increasing overlap.² For these materials the variation of H_{iso} on going from the sulfide to the selenide is consistent with the expected increase in covalency. In Table I the magnitude of H_{iso} for the Hg and Cd chromium sulfides or selenides is noted to increase with increasing nonmagnetic cation atomic number. The invariance of the lattice parameters for these sulfides and selenides indicates overlap constancy within each pair of compounds. This constancy clearly allows us to associate the variation in H_{iso} with increasing covalency for increasing atomic number of the nonmagnetic cation. The different u parameter⁹ for ZnCr_2Se_4 makes a detailed comparison with the other compounds tenuous. However, inclusion of H_{iso} for ZnCr_2Se_4 in Fig. 1 more strikingly demonstrates this systematic variation of covalency for the selenides. The proportionality of H_{iso} and J taken in conjunction with the opposing effects on these parameters by overlap contributions leads us to three conclusions. Firstly, chromium-chalcogen and chromium-chromium overlap differences between these compounds are small. Secondly, the systematic variation of covalency in these compounds gives rise to the observed proportionality between H_{iso} and J . Finally, our data lend support to the theoretical treatment of the nn exchange carried out by Huang and Orbach.⁴

Also included in Fig. 1 are data for the chromium trihalides.¹⁰⁻¹² A similar linear dependence of H_{iso} on

⁷ Evidently, the normally cubic symmetry of the tetrahedral spinel A site has been reduced in this spiral antiferromagnet. We conclude that only the magnetic symmetry has been significantly reduced since no electric quadrupole splitting for ^{201}Hg nuclei with $I = \frac{3}{2}$ has been recognized. This reduction of symmetry is consistent with the proposed magnetic structure of J. M. Hasting and L. M. Corliss, *J. Phys. Chem. Solids* **29**, 9 (1968). The H_{iso} quoted in Table I for Hg in HgCr_2S_4 is the field corresponding to the high-frequency peak. This approximation will in no way effect our conclusions.

⁸ O. Matamura, *J. Phys. Soc. Japan* **14**, 108 (1959).

⁹ P. K. Baltzer, M. Robbins, and P. J. Wojtowicz, *J. Appl. Phys.* **38**, 953 (1967).

¹⁰ A. C. Gossard, V. Jaccarino, and J. P. Remeika, *Phys. Rev. Letters* **7**, 122 (1961). H_{iso} for CrBr_3 .

¹¹ A. Narath, *Phys. Rev. Letters* **7**, 410 (1961). H_{iso} for CrCl_3 .

¹² A. Narath, *Phys. Rev.* **140**, A854 (1965). H_{iso} for CrI_3 and J_t for all CrX_3 .

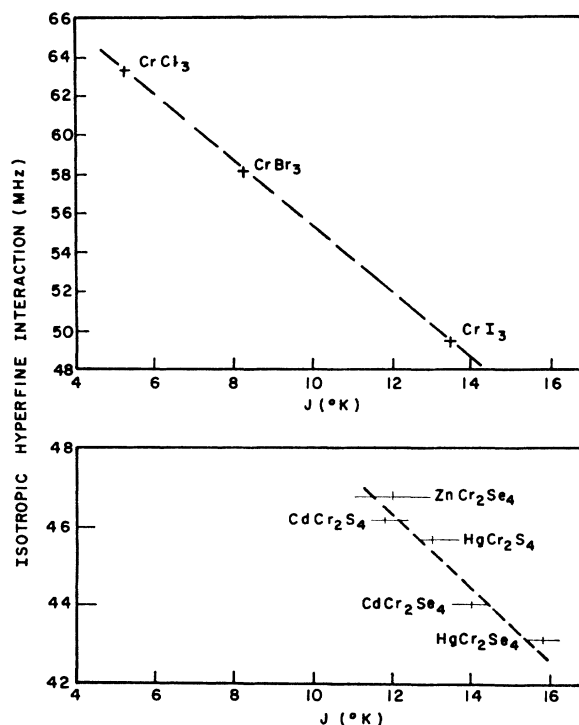


Fig. 1. Plot of the isotropic hyperfine interaction for ^{53}Cr (proportional to H_{iso}) as a function of the nn exchange parameter J for the compounds noted. The horizontal bars are representative of the uncertainty in J .

J is noted. The different slopes for the two systems reflect the different contributions of the important exchange paths to J . In addition, the overlap contributions to J while apparently constant for each system, need not be the same for the different types of compounds.

The large negative H_{iso} for ^{77}Se given in Table I for the spinels can be contrasted with the large, but positive, hyperfine interaction found in MnSe .³ Covalent mixing of the valence s orbitals of the anion with the transition metal $3d e_g$ orbitals can explain both observations. For Mn^{2+} , the $3d e_g$ orbitals are half-filled with electrons of spin parallel to those in the half-filled t_{2g} orbitals. Covalent mixing of valence electrons into the spin antiparallel e_g orbitals will result in a positive Se hyperfine interaction. On the other hand, for Cr^{3+} the $3d e_g$ orbitals are empty. One can expect the hyperfine interaction to

TABLE I. Isotropic hyperfine fields and exchange parameters for chromium chalcogenide spinels.

Compound	Isotropic hyperfine field (kOe)			J^a (°K)	K^a (°K)
	Cr	Se	Cd		
CdCr_2S_4	-182.0		+168.10	11.8	-0.3
CdCr_2Se_4	-200.0	-97.8	+136.41	14.0	-0.1
HgCr_2S_4	-189.9 ^b		+524.3	13.0	-0.6
HgCr_2Se_4	-179.4	-91.7	+446	15.8	-0.5

^a See Ref. 1.

^b S. B. Berger, T. J. Burch, and J. I. Budnick, *Bull. Am. Phys. Soc.* **13**, 474 (1968).

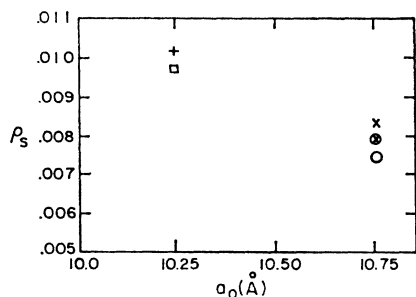


FIG. 2. Plot of the valence s -shell spin density on the nonmagnetic cation as a function of the lattice parameter for CdCr₂S₄ (+), HgCr₂S₄ (□), CdCr₂Se₄ (⊗), and HgCr₂Se₄ (○). ⊗ refers to both the Cd and the Hg ρ_s , which are equal, in Cd_{0.7}Hg_{0.3}Cr₂Se₄.

be negative in this case if the energy separation between the exchange split e_g spin-parallel and -antiparallel levels is the determining factor for the covalency. It appears that the contribution to H_{iso} from this covalency for Cr³⁺ will be negative even without this restriction.¹³ The contribution to J by this covalent admixture has been computed to be small compared to that resulting from a mechanism involving spin polarization of Se orbitals by the Cr $3d$ electrons.⁴ For this reason we prefer to explain the negative Se hyperfine interaction in terms of a spin polarization of the s Se orbitals by the $3d$ Cr electrons. This contribution to H_{iso} depends on the Cr to Se interionic distance and the Se and Cr wave-function shapes, which because of the identical lattice parameters are expected to be very nearly the same for CdCr₂Se₄ and HgCr₂Se₄. There are other contributions to H_{iso} , namely, positive ones arising from overlap of the half-filled t_{2g} orbitals of Cr with Se orbitals and covalent mixing of spin-antiparallel Cr t_{2g} and Se orbitals. These terms are expected to be small since the Se s orbitals do not mix with Cr t_{2g} orbitals to first order. The overlap contribution should be similar for the two compounds, whereas, the positive covalency contribution should be greater for HgCr₂Se₄ as indicated by our Cr NMR results. The sum of these contributions would account for the observed larger magnitude of the ⁷⁷Se H_{iso} for CdCr₂Se₄.

¹³ J. Danon, H. Panepucci, and A. Missetich, J. Chem. Phys. 44, 4154 (1966); R. E. Watson and A. J. Freeman, Phys. Rev. 134, A1526 (1964).

The valence s -shell spin density ρ_s of the nonmagnetic cation has been obtained by dividing H_{iso} for Cd and Hg in these compounds by the splitting parameter A for the lowest ²S monovalent free-ion level.^{14,15} The sign of H_{iso} indicates that the spin on this cation is parallel to the sample magnetization. Figure 2 contains a plot of ρ_s as a function of a_0 , the lattice parameter. The Cr-nonmagnetic-ion internuclear distance is proportional to a_0 . The general decrease in H_{iso} with chalcogen (S or Se) atomic number or increasing a_0 indicates that covalency contributions to H_{iso} are overwhelmed by those from overlap. There is a similar variation in K , given in Table I, with a_0 which suggests to us an interrelated origin. For example, an antiferromagnetic- nnn exchange path involving direct overlap of Cr t_{2g} orbitals and empty nonmagnetic cation orbitals is possible. This path is consistent with, though not necessitated by, our data and more closely resembles that contemplated in Ref. 1 than that considered elsewhere.¹⁶

The difference in ρ_s for the Cd and Hg compounds is believed to be real in spite of the approximation of using the free-ion value of A . We note that the ρ_s for both Cd and Hg in the mixed compound Cd_{0.7}Hg_{0.3}Cr₂Se₄ are identical, and reflects a linear variation of ρ_s with composition. Since the overlap should be constant for compounds with the same a_0 , the data in Fig. 2 imply that there is an additional contribution to ρ_s which can be, for example, a negative term related to covalency.

The comprehensive study of the hyperfine interactions in this magnetic system has led to a detailed and consistent explanation of the hyperfine interactions at the different sites. Through this, a significant substantiation of the specific nn exchange path and an indication of a nnn exchange mechanism responsible for the difference in the bulk magnetic properties of these compounds has been established by these experiments.

The authors are grateful to Dr. H. L. Pinch for the preparation and x-ray characterization of the samples used.

¹⁴ F. M. Kelley and J. B. Sutherland, Can. J. Phys. 34, 521 (1956).

¹⁵ S. Mrozowski, Phys. Rev. 61, 605 (1942).

¹⁶ For example, K. Dwight and N. Menyuk, Phys. Rev. 163, 435 (1967).