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### EVIDENCE FOR ITINERANT *d*-ELECTRON FERROMAGNETISM

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We describe here a metallic ferromagnetic system  $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$  and  $\text{Co}_{1-x}\text{Ni}_x\text{S}_2$  that appears to have a single doubly degenerate band. The electrons in the band are itinerant as manifested by metallic electrical conductivity, but the magnetic moment is that of the isolated ion.

For several decades localized as opposed to itinerant-electron ferromagnetism in metals has been investigated theoretically.<sup>1</sup> However, experimental systems on which to base theoretical models of band ferromagnetism are often complicated by the presence of composite bands as, for example, in the elemental transition metals which are comprised of overlapping broad *s* and narrow *d* bands. Such quantities as density and itinerancy of *d* electrons, magnetization of the *s* electrons, and the magnitude of *s-d* exchange are difficult to measure directly. The compounds to be discussed appear to avoid the complicating features introduced by the presence of such *s* electrons.

All transition metal disulfides,  $\text{FeS}_2$  through  $\text{ZnS}_2$ , crystallize in a cubic pyrite structure in

which the cations are in face-centered positions. The physical properties of the series<sup>2</sup> are summarized in Table I. Each successive member of the series represents the progressive addition of one *d* electron. In much of this series, a continuous range of solid solutions of adjacent members, e.g.,  $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$  and  $\text{Co}_{1-x}\text{Ni}_x\text{S}_2$  for  $0 \leq x \leq 1$ , can be formed.<sup>3</sup> The unit cell dimension increases monotonically with increasing atomic number of the cation. These solid solutions are metallic conductors<sup>4</sup> (Fig. 1) except for dilute concentrations (<0.1%) of  $\text{CoS}_2$  in either  $\text{FeS}_2$  or  $\text{NiS}_2$ .

Since the beginning and end members of the series are both semiconducting while all other members (except near  $\text{NiS}_2$ ) show metallic conductivity, it is not inconsistent to conclude that

Table I. Magnetic and transport properties of pyrite compounds.

$\text{FeS}_2$	Temp. independent paramagnetic $\chi = 0.31 \pm .04 \times 10^{-6}$ emu/gm	Semiconductor $\Delta E = 0.92 \pm .05$ ev	$\Delta E = 0.96 \pm .02$ ev	$t_{2g}^6$
$\text{CoS}_2$	Ferromagnetic $\mu_s = 0.9 \mu_B$ ; $T_c = 120^\circ\text{K}$ $g^2 S(S+1) = \begin{cases} 4.05 \pm .05 \mu_B^2 & T > 400^\circ\text{K} \\ 3.29 \pm .05 \mu_B^2 & T < 400^\circ\text{K} \end{cases}$	Metallic	Plasma Edge $\sim 1.0$ ev	$t_{2g}^6 e_g$
$\text{NiS}_2$	Paramagnetic $g^2 S(S+1) = 11.0 \pm 1.6 \mu_B^2$	Semiconductor $\Delta E = 0.22$ ev $T < 420^\circ\text{K}$ $\Delta E = 0.64$ ev $T > 420^\circ\text{K}$		$t_{2g}^6 e_g^2$
$\text{CuS}_2$	Pauli Paramagnetic $\chi \approx 0.29 \times 10^{-6}$ emu/gm	Superconducting $T_c = 1.51 \approx .02^\circ\text{K}$	Plasma Edge $\sim 1.6$ ev	$t_{2g}^6 e_g^3$
$\text{ZnS}_2$	Diamagnetic $\chi \approx -0.36 \times 10^{-6}$ emu/gm	Extrinsic semiconductor $\Delta E \sim 2.5$ ev		$t_{2g}^6 e_g^4$

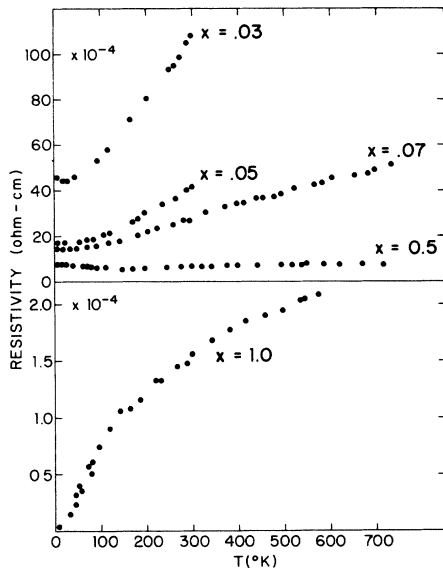


FIG. 1. Resistivity of single crystals of  $Fe_{1-x}Co_xS_2$ . Note the decrease in resistivity with increase of electron concentration in the conduction band. The crystal  $x = 0.5$  is two phase with Fe/Co ratios about 10% on either side of stoichiometry. The semiconductivity at low temperature may be caused by electron scattering at the phase boundary.

the  $3d e_g$  electrons occupy a band of exactly four states isolated by energy gaps from both a lower filled band and an empty higher-energy antibonding band and that these  $d$  electrons are itinerant.

The semiconductivity of  $NiS_2$  is consistent with

the notion of a narrow energy band with strong electron correlation. This compound is midway in the series and possesses two  $3d e_g$  electrons. Thus the proposed conduction band is expected to be exactly half full. It has been suggested<sup>5</sup> that the pseudoparticle spectrum of a half-filled band sufficiently narrow compared with the intra-atomic interaction splits into two bands, the lower of which becomes filled, and the system behaves as an insulator (or a semiconductor).

The existence of a continuous range of solid solutions permits continuous variation of the average number  $n$  of  $3d e_g$  electrons per cation in the band without encountering changes in crystal structure that would introduce large perturbations on the band structure. Thus, for  $Fe_{1-x}Co_xS_2$ ,  $n = x$ , and for  $Co_{1-x}Ni_xS_2$ ,  $n = 1 + x$ . The value of a single band is that variation in  $n$  does not introduce redistributions of occupancy between overlapping bands as must occur, for example, in an alloy series of transition-metal elements. Thus, the development and disappearance of ferromagnetism can be observed as  $n$  increases from zero to greater than unity without major perturbations introducing subsidiary effects.

The saturation magnetization  $\mu_s$  obtained by extrapolation to infinite magnetic field ( $1/H \rightarrow 0$ ) and zero temperature for  $Fe_{1-x}Co_xS_2$  is shown in Fig. 2. Over the range  $0.1 \leq x \leq 0.95$ , the saturation magnetization in Bohr magnetons is proportional to cobalt concentration ( $\mu_s = xg_{Co}S_{Co}\mu_B$ ),

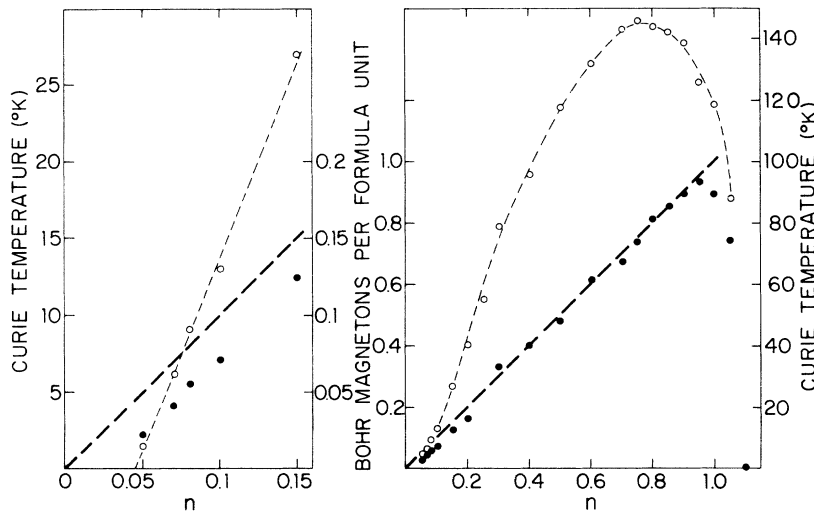


FIG. 2. Spontaneous magnetization  $\mu_s$  and Curie temperature  $T_c$  versus electron concentration  $n$ . Closed circles:  $\mu_s$  (Bohr magneton per formula unit). Open circles:  $T_c$  ( $^{\circ}K$ ). A line  $\mu_s = n$  is drawn to show the scatter of data points around the condition for complete magnetization as well as the trend to lower saturation magnetization at small and large values of  $n$ .

indicating that all  $3d e_g$  electrons magnetize. Long-range order characterized by a sharply decreasing magnetization near the Curie temperature  $T_C$  occurs for  $0.1 \leq x \leq 1.0$ , the lower limit corresponding approximately to an average of one nearest-neighbor cobalt. The variation of  $T_C$  with  $n$  is also given in Fig. 2.

For  $x \leq 0.1$ , it is difficult to establish true ferromagnetism. Magnetization does not descend sharply to zero at  $T_C$  and does not saturate at the highest applied fields (16 kOe). The remanence is zero within experimental error. However, if  $T_C$  is defined as the temperature at which the initial permeability in a 1-Oe field peaks sharply, usually denoting the onset of domain formation and the development of magnetic anisotropy,  $T_C$  can be extended below  $x = 0.1$ . Such a definition suggests that ferromagnetism occurs at dilutions as low as  $x = 0.05$ . The saturation magnetization shown in the left of Fig. 2 is less than that expected for complete magnetization of the spins. However, the lack of near saturation at the highest applied fields makes the quoted saturation value obtained by extrapolation to infinite field very doubtful.

The square of the effective paramagnetic moment  $p_{\text{eff}}^2$  obtained from high-temperature susceptibility measurements increases linearly with cobalt concentration. The break in the plot of reciprocal susceptibility of  $\text{CoS}_2$  versus temperature at  $400^\circ\text{K}$ <sup>6</sup> has been found to be associated with a transition that is also manifested by an abrupt change in the temperature dependence of both the electrical resistivity and unit cell dimension. Therefore, the high-temperature value of  $p_{\text{eff}}^2 = 3.3 \mu_B^2$  may not be indicative of the low-temperature electronic state of  $\text{CoS}_2$ . This break is not seen in  $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$  for  $x \leq 0.9$  for which the value of  $p_{\text{eff}}^2$  after correction for the susceptibility of the  $\text{FeS}_2$  host is  $3.9 \mu_B^2/\text{cobalt ion}$ . No exchange-enhanced susceptibility marking the onset of ferromagnetic order was found at any concentration as observed, for example, in the Ni-Rh alloys.<sup>7</sup>

The linear dependence of saturation magnetization with concentration ceases near 0.95, and for higher cobalt concentrations, the magnetization decreases to  $0.9 \mu_B$  for  $\text{CoS}_2$  ( $n = 1$ ). Neutron diffraction results indicate that the spin configuration of  $\text{CoS}_2$  is collinear.<sup>8</sup> If the reduced moment were due to a conical spiral, an apex angle of  $25^\circ$  would be necessary to account for the 10% reduction in moment. It seems probable that such a large angle would have been detected had

it existed. More likely is the possibility that the energy separation between up- and down-spin bands is smaller than the Fermi energy for  $n > 0.95$  in the up band alone, and the down-spin band becomes occupied at the higher concentrations.

The average number of electrons in the band may be extended beyond unity by forming the solid solutions  $\text{Co}_{1-x}\text{Ni}_x\text{S}_2$ . The saturation magnetization for these compositions, shown in Fig. 2 for the region of  $n > 1.0$ , continues to decrease, the magnetization disappearing for  $x = 1.1$  at which value  $T_C$  approaches zero. For  $n > 1.1$ , the solid solutions may be antiferromagnetic, although no well-defined Néel temperature can be observed. The measured susceptibility of  $\text{Co}_{1-x}\text{Ni}_x\text{S}_2$  is in agreement with that calculated by scaling the susceptibility of the individual ions in proportion to their concentration,  $p_{\text{eff}}^2 = 3.9(1-x) + 11.0x$ . The susceptibility of  $\text{NiS}_2$  ( $x = 1$ ) gives  $g_{\text{Ni}} = 2.34$  assuming  $S_{\text{Ni}} = 1$  in good agreement with the value for a  $\text{Ni}^{+2}$  ion; however, the Weiss constant  $\theta = -1800 \pm 200^\circ\text{K}$  is unusually large. For the compounds  $\text{Co}_{1-x}\text{Ni}_x\text{S}_2$ , the Weiss constant increases negatively very nearly proportionally to Ni concentration. A possible explanation for the absence of magnetic order is that the nearest-neighbor correlation is very large but the next-nearest-neighbor interaction, which is required to produce a long-range antiferromagnetic order in a fcc lattice,<sup>9</sup> is so small that ordering takes place only at very low temperatures, if at all.

Despite the apparent itinerancy of the  $d$  electrons giving rise to metallic electrical conductivity, magnetic moments agree well with that expected for an isolated divalent ion. Further experimental evidence for localization is obtained from  $\text{Co}_{0.75-2x}\text{Ni}_x\text{Fe}_{0.25+x}\text{S}_2$ , which is a quaternary solid solution that holds the total number of  $3d e_g$  electrons constant at 0.75. Here, unlike  $\text{CoS}_2$ , all spins of the starting composition  $\text{Co}_{0.75}\text{Fe}_{0.25}\text{S}_2$  are magnetized ferromagnetically. As the Ni content increases,  $p_{\text{eff}}^2$  again scales in proportion to the concentration of magnetic ions, but the saturation magnetization decreases as  $[(0.75-2x)g_{\text{Co}}S_{\text{Co}} - xg_{\text{Ni}}S_{\text{Ni}}] \mu_B$  for  $0 < x < 0.1$ . Assuming strong localization of the cation spins, the two electron spins on  $\text{Ni}^{+2}$  half fill its  $e_g$  orbital, and the exclusion principle requires that intra-atomic correlation with an itinerant up spin at the Ni site will occur only when the Ni spins are antiparallel to the itinerant spin. For  $x > 0.1$ , the saturation magnetiza-

tion decreases less rapidly with  $x$ , probably reflecting the onset of Ni-Ni interactions.

These data provide strong evidence for the existence of itinerant electrons with localized magnetic moments. Several questions remain unresolved: the nature of the magnetic state in a random solid solution at concentrations lower than one cobalt in every nearest neighbor on the average; the absence of an exchange-enhanced susceptibility; the decrease in  $\mu_S$  for  $0.95 < n < 1.0$ ; and the unusually large Weiss constant for solid solutions containing nickel. It appears, however, that magnetic systems such as the one described here provide a unique opportunity to study ferromagnetism unencumbered by the complexities of conventional ferromagnetic metals.

We wish to thank D. B. Rogers for many help-

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<sup>4</sup>Resistivities of FeS<sub>2</sub>, CoS<sub>2</sub>, NiS<sub>2</sub>, and CuS<sub>2</sub> are given in Ref. 3.

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#### HIGH-DEGREE EXCHANGE INTERACTION BETWEEN RARE-EARTH IONS

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From the EPR spectra of pairs of Ce<sup>3+</sup> and Nd<sup>3+</sup> ions in LaCl<sub>3</sub> and LaBr<sub>3</sub> it is possible to isolate contributions to the interaction tensors from high-degree anisotropic superexchange interaction of the form  $J_+^5(1)J_-^5(2)$  and  $J_z^l(1)J_\pm^5(2)$ .

Recently there has been a considerable amount of theoretical speculation concerning the possibility of anisotropic interactions of high degree in the angular momentum operators between ions whose orbital moments are not quenched.<sup>1-5</sup> These interactions may arise either from the electrostatic coupling between the electric multipole moments of the two atoms or from a more general form of exchange interaction in which one allows the exchange coupling to depend on the orbitals involved. With a few notable exceptions,<sup>6,7</sup> however, there is almost no detailed experimental information available on such systems. In this Letter we report new measurements on the interactions between the ground-state doublets of Ce<sup>3+</sup> pairs in LaBr<sub>3</sub> and Nd<sup>3+</sup> pairs in LaCl<sub>3</sub> and LaBr<sub>3</sub>,<sup>8</sup> using the technique of EPR of pairs of coupled ions. In addition, we present a reanalysis of some previous results on Ce<sup>3+</sup> pairs in LaCl<sub>3</sub>.<sup>9</sup> By making a detailed comparison of the  $g$  tensors and interaction tensors for both the nearest-neighbor (nn) and next-nearest-neighbor (nnn) pairs in all four systems it is possible to isolate contributions from superexchange terms of the form  $J_+^5(1)J_-^5(2)$  and  $J_z^l(1)J_\pm^5(2)$ . We believe that this is the first ex-

PLICIT measurement of such high-degree terms. In addition it is found that there is unambiguous evidence for electric quadrupole-quadrupole (EQQ) interaction between the Ce<sup>3+</sup> ions, and that the higher-rank electric multipole interaction (EMI) terms are significantly smaller than the EQQ.

The total spin Hamiltonian for a pair of identical Kramers doublets in a magnetic field  $\vec{H}$  is given by:

$$\mathcal{H}_{ij} = \mu_B \vec{H} \cdot g \cdot \vec{S}_i + \mu_B \vec{H} \cdot g \cdot \vec{S}_j + \vec{S}_i \cdot \mathbf{K}_{ij} \cdot \vec{S}_j, \quad (1)$$

where  $\vec{S}_i$  and  $\vec{S}_j$  are effective spin- $\frac{1}{2}$  operators. Using EPR one can measure the  $g$  tensor and the traceless part  $\mathbf{A}$  of the tensor  $\mathbf{K}$ . The components of these tensors which we were able to measure in the experiments, carried out mainly at 36 Gc/sec and 4.2°K, are summarized in Table I. In certain cases, values for the additional components of  $\mathbf{K}$  may be deduced by combining the pair results with the measured bulk properties of the concentrated material.<sup>10</sup> In particular, such an analysis for Ce<sup>3+</sup> gives  $K_{zz}^{\text{nnn}}$