fits stem from the assumption that the number of Bloch walls pinned at temperature T is described by a Lorentzian function. Although this assumption is quite plausible, it would be reckless to view the agreement as a verification of the theory.

If the spacing of the Bloch walls at T_C is $\lesssim 10^{-4}$ cm for a sample with a 1-cm^2 cross section, then $n(\kappa_0) \gtrsim 10^4$ walls/cm^3. Galt *et al.*[15] measured the frequency dependence of the initial permeability in magnetite (Fe_3O_4) and in $NiFe_2O_4$, and deduced appreciably different values of β for the two samples, 0.406 and 0.026 g cm^{-2} sec^{-1}, respectively. If $\beta \approx 1.0$ g cm^{-2} sec^{-1} represents an upper limit on the damping constant, then one could assume that $n/\beta \gtrsim 10^4$ for Dy and Tb samples. We can, therefore, infer from the values of nf/β given in Table I that the Tb absorption was nearly on-resonance ($f \approx 1$) in zero applied field, whereas the Dy absorption was far off-resonance ($f \ll 1$) in zero applied field. Apparently, application of the magnetic field in Dy causes changes in m_0, β, and κ_0, such that the domain walls are more nearly brought into resonance with the sound wave. This possible explanation of the seemingly contradictory zero-field observations is, of course, pure speculation. Further theoretical interpretation must await a careful investigation of the spectral dependence of the attenuation.

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Nickel Sulfide—an Itinerant-Electron Antiferromagnet

J. M. D. Coey and R. Brusetti
Transitions de Phases, Centre National de la Recherche Scientifique, 38042 Grenoble-Cédex, France

and

A. Kallel
Département de Physique, Université de Tunis, Tunis, Tunisia

and

J. Schweizer and H. Fuess
Institut Lauë-Langevin, 38042 Grenoble-Cédex, France

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Antiferromagnetic nickel sulphide has a small temperature-independent magnetic susceptibility. The ordered moment per nickel atom, measured with neutrons, decreases from $1.45\mu_B$ to $1.00\mu_B$ at 4.2 K with a decrease of 0.6% in the Ni-Ni distance. These data indicate a band model for the 3*d* electrons, making NiS an itinerant-electron antiferromagnet with no local moments. The possibility of local moments in an antiferromagnetic metal is briefly discussed.

The existence of itinerant-electron antiferromagnetism has been established with certainty in only a few materials, notably chromium metal.[1] An antiferromagnetic metal is predicted as an intermediate state between the antiferromagnetic insulator and the Pauli-paramagnetic metal as

some parameter such as the lattice constant or the intra-atomic Coulomb interaction is varied.[2] Nevertheless, it does not occur in the most extensively studied metal-insulator transition system $(V_{1-x}Cr_x)_2O_3$,[3] probably because the jump in the lattice parameter at the transition is such that the itinerant-electron antiferromagnetic state would appear in the "lost volume."[4] In this Letter, we present evidence to show that nickel sulphide is an itinerant-electron antiferromagnet below its first-order magnetic ordering temperature[5] T_t, changing to a metal with a very short spin-spin correlation time above T_t. Our susceptibility and neutron-diffraction data below the transition seem incompatible with the presence of local moments on the nickel sites, assumed by previous workers,[6,7] although above T_t we confirm White and Mott's interpretation of NiS as a normal d-band metal.[6]

A semimetallic or metallic conductivity might be considered as evidence that an antiferromagnet is itinerant-electron type, but this condition is insufficient because the conduction electrons are not necessarily the magnetic electrons. The conductivity, shown in Fig. 1(a), is substantially independent of temperature below T_t, in agreement with earlier work.[7,8] It would be consistent with NiS being either a degenerate semiconductor or a semimetal below T_t although the electronic-specific-heat coefficient, $\gamma = 0.9 \pm 0.4$ mJ/mole K^2,[9] favors the semimetallic interpretation. Above T_t the conductivity has a normal metallic temperature dependence. To show that NiS is an itinerant-electron antiferromagnet, it is sufficient to show that the magnetic electrons are itinerant. We do this by pointing out that the susceptibility is inconsistent with the existence of $S \simeq 1$ local moments, and that the ordered moment varies as a function of cell parameter to an extent highly unlikely if the moments are localized.

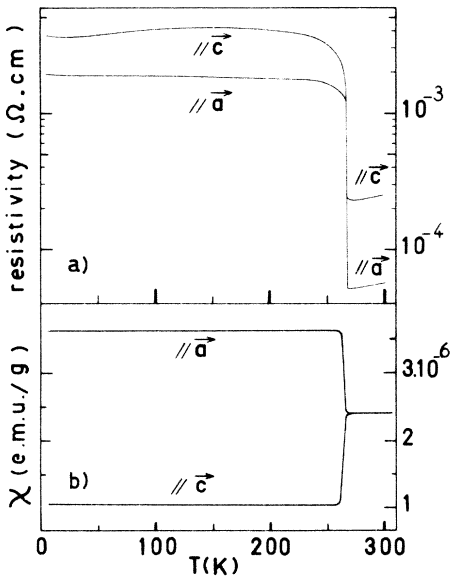

FIG. 1. Temperature dependence of (a) the conductivity and (b) the magnetic susceptibility of a stoichiometric crystal of hexagonal nickel sulphide.

Our first evidence in favor of a band model for the nickel moments is provided by the susceptibility, Fig. 1(b): Both $\chi_\parallel$ and $\chi_\perp$ are remarkably independent of temperature in the antiferromagnetic phase. If $\chi_\parallel(T) - \chi_\perp(T)$ is fitted with the standard local-moment model,[10] the extrapolated Néel temperature would be ~1600 K, implying unprecedented superexchange interactions. However, both the nickel moment[5] and the hyperfine field on ^{57}Fe impurities[11] decrease by 10% in the range $0 < T < T_t$, giving an extrapolated Néel temperature of only ~400 K if local moments are assumed.[11,12] The inconsistency vanishes with a band model. The simplest is the Stoner-Lidiard model.[13] The intersublattice exchange, which we assume to be dominant, is determined to be $k\theta' \simeq 0.18$ eV from the temperature dependence of the nickel sublattice magnetization and its reduced value at $T = 0$, $\xi_0 \simeq 0.7$. The perpendicular susceptibility is given by

$$\chi_\perp = N_0 \mu_B^2 / k\theta',$$

where N_0 is the number of electrons in the magnetically polarized band (two per nickel atom). The calculated value is $\chi_\perp = 3.96 \times 10^{-6}$ emu/g, in good agreement with observation [Fig. 1(b)]. The parallel susceptibility, unlike the perpendicular susceptibility, depends on the form of the density of states which is not yet known with any certainty in NiS. Nevertheless, it should be rather independent of temperature, and tend to a nonzero value as $T \to 0$.[13] The recent theory of Brandt and Gross[14] for itinerant-electron antiferromagnets also predicts that $\chi_\perp$ varies little between $T = 0$ and T_N provided there is no Hubbard *gap* at $T = 0$. This is consistent with the semimetallic behavior below T_t. The spin-wave dispersion relation for NiS was found to be very steep,[15] and also implies a very high extrapolated Néel temperature if interpreted on a local-moment model. As it appears this is not the case[11,12], the stiff spin waves should rather be regarded as evidence for itinerant-electron antiferromagnetism.[15]

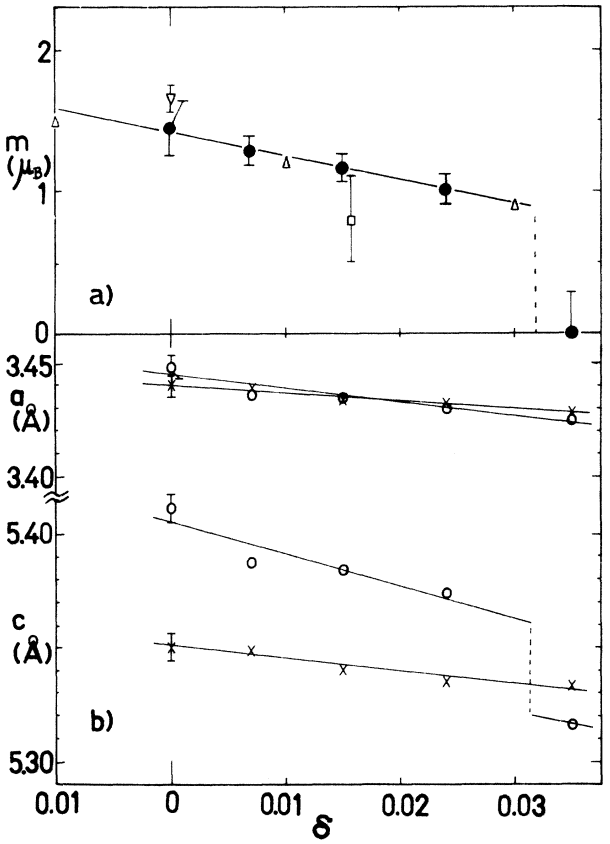

FIG. 2. (a) Variation of the magnetic moment of $Ni_{1-\delta}S$ at 4.2 K as a function of stoichiometry deriving δ from the transition temperature. Circles, this work; inverted triangle, Ref. 5; triangles, Ref. 18; square, Ref. 15. (b) Variation of the lattice parameters of $Ni_{1-\delta}S$ as a function of stoichiometry. Crosses, 296 K; circles, 4.2 K.

Our second evidence in favor of a band model follows from neutron-diffraction powder patterns which provided us lattice parameters and magnetic moments for a series of five samples $Ni_{1-\delta}S$ of differing stoichiometry, $0<\delta<0.045$. The homogeneity of each of the first four samples was deduced from the width of the specific-heat anomaly at T_t ($\lesssim 10$ K) to be better than ± 0.001 in δ. The nonstoichiometry takes the form of vacancies on the nickel lattice,[16] and has the effect of reducing the lattice parameters, particularly in the c direction. This appears rather clearly in Fig. 2(b), although neutron diffraction is not the most precise technique for lattice-parameter determinations. Moreover there seems to be an abrupt decrease in c near $\delta=0.03$ at 4.2 K associated with loss of moments [Fig. 2(a)]. The moments are derived from (101) and (111) reflections at 4.2 K, the only ones with any substantial magnetic contribution, using the Ni^{2+} form factor.[17] These contributions have been normalized using the nuclear intensities of the first ten reflections. At least two diagrams were taken for each sample, and the errors given are twice the standard deviation of the average of the moments derived from each magnetic reflection. Some other values of the moment, taken from the literature,[5,15,18] are also included in Fig. 2(a). Such sensitivity of a band moment to interatomic distance is not surprising, particularly if the band is partially split because of a Mott-Hubbard interaction.[2] On the contrary, a localized moment can only vary with lattice parameter if there is a large orbital contribution, or possibly because of covalency effects. Orbital effects are ruled out because they would tend to increase the nickel moment beyond its spin-only value of $2\mu_B$, whereas the moment in fact is a lot smaller. As for covalence, it seems quite implausible that the increased p-d mixing due to a 0.4% change in the Ni-S distance could reduce the moment by as much as one third. Data on the five samples of $Ni_{1-\delta}S$ are shown in Table I.

In brief, it appears that a coherent picture of the antiferromagnetic phase is impossible if local moments are assumed, and that the above results require a band model.

In another experiment, we have also examined NiS powder in the metallic phase, above T_t, with polarized neutrons. The aim was to measure the incoherent magnetic scattering, and place a limit on the disordered moment in the paramagnetic state. We found that the incoherent magnetic scattering was independent of scattering vector, and that the standard deviation on the four points measured required a moment less than $0.53\mu_B$. This result should be compared with the exchange splitting of the nickel $3s$ shell found with electron spectroscopy for chemical analysis (ESCA),[19] which corresponds to a moment of $(1.5\pm0.2)\mu_B$. The two results can only be reconciled if the spin-spin correlation time for the electrons at the nickel site lies between the characteristic times of the two measurements. These are given by the time of passage of a neutron over an atomic distance, and the width of the $3s$ level, 10^{-13} sec and 10^{-16} sec, respectively. We deduce that the correlation time is of order 10^{-14} or 10^{-15} sec in metallic nickel sulphide. The time corresponding to a $3d$ bandwidth of 1 eV is also of order 10^{-15} sec, and it should be similar to or longer than the correlation time in a nonmagnetic metal.

No inferences can be made about the electronic

TABLE I. Data on five samples of $Ni_{1-\delta}S$.

δ	Moment at 4.2 K (μ_B)	Transition temperature (K)	Ni-Ni (Å)	Ni-S (Å)
0.000	1.45 ± 0.20	264 ± 5	2.702 ± 0.005	2.402 ± 0.005
0.007	1.29 ± 0.10	240 ± 5	2.694 ± 0.005	2.398 ± 0.005
0.015	1.17 ± 0.10	196 ± 5	2.692 ± 0.005	2.397 ± 0.005
0.024	1.00 ± 0.10	146 ± 6	2.687 ± 0.005	2.393 ± 0.005
0.035	$0.00 \pm {}^{+0.30}_{-0.00}$	...	2.659 ± 0.005	2.383 ± 0.005

properties of the antiferromagnetic state from measurements in the paramagnetic state because they are different phases, separated by a first-order transition.

We have argued here that nickel sulphide is an itinerant-electron antiferromagnet because the magnetic electrons are delocalized, and must be described by a band model. However, the breakdown of the Mott insulating state does not inevitably require the disappearance of local, Hund's-rule moments. When the electrons are delocalized for only a small fraction of the time, remaining highly correlated for most of the time, an antiferromagnetic metal with quite different magnetic properties from NiS results. A possible example is FeS, where the low-lying α-spin electrons are localized, and perhaps only the single β-spin electron at the top of the band is itinerant. A transition from local-moment to band-moment behavior in the antiferromagnetic metal with decreasing lattice parameter is conceivable, though no example is known to the authors.

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