

Heat capacity of nickel sulfide and its semimetal-metal transition

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Heat-capacity measurements have been made from 5 to 330 K on NiS which shows a nonmetal-metal transition at 265 K, and on Ni_{0.95}S which is metallic at all temperatures. The low-temperature data yield electronic specific-heat coefficients of 0.9 ± 0.2 and 6.2 ± 0.4 mJ/mole K² and characteristic temperatures of 373 and 336 K, respectively. We deduce that NiS is a semimetal, not a semiconductor, at low temperatures. Of the entropy of transition, 5.32 J/mole K, 25% is electronic and 75% is due to the lattice. Any magnetic contribution is small compared to $R \ln(2S + 1)$. The entropy of transition is proportional to the transition temperature T_t for a series of samples with $105 < T_t < 315$ K. A strong electron-phonon interaction is indicated. Structure in the specific-heat anomaly of tiny crystals (~ 1 mg) is ascribed to the presence of domains of dimensions ~ 100 μm with slightly different stoichiometries.

INTRODUCTION

Hexagonal nickel sulfide exhibits a metal-nonmetal transition which has aroused considerable interest since its discovery in 1967 by Sparks and Komoto.¹ The principal experimental result is that NiS passes from an antiferromagnetic state to a more conducting state with a Pauli-type susceptibility at $T_t = 265$ K.² The transition temperature is very sensitive to stoichiometry^{2,3} and external pressure.^{4,5}

It is thought that the transition is first order because of a 1.9% volume change at T_t .⁶ Furthermore, several other physical parameters fall abruptly, including the resistivity,¹ susceptibility,⁷ nickel moment,² and the hyperfine field and isomer shift measured on ⁵⁷Fe impurities by the Mössbauer effect.^{8,9} In spite of all this, the crystal structure does not change,⁵ and α NiS belongs to a small group of materials with coincident electric and magnetic transitions at some temperature, but no change of symmetry (cf. EuO, Cr). Adler¹⁰ suggested in 1968 that the transition was basically magnetic in origin.

Before a satisfactory model of the transitions can be developed, it is necessary to define experimentally the electronic structure of the high- and low-temperature phases. Various suggestions have so far been advanced. At first Sparks and Komoto proposed a semiconductor-metal transition on the basis of their conductivity measurements on powders.¹ Subsequently, White and Mott¹¹ interpreted the extensive single-crystal transport and magnetic measurements of Townsend *et al.*¹² as showing that the transition was from semimetal to metal. Andreev *et al.*¹³ interpret similar data as favoring a semiconductor-semimetal transition.

Heat-capacity measurements were previously made in the range 35–300 K on a stoichiometric sample.¹⁴ These data showed some of the characteristics of a first-order transition with an entropy change of 5.03 J/mole K, but no conclusion was

drawn concerning a possible change in C_p at the transition. A comparable entropy change has been reported in differential thermal analysis.¹⁵

On the basis of a variety of magnetic evidence, we have argued that NiS is an itinerant antiferromagnet with band moments below T_t and a normal nonmagnetic metal above.^{16,17} In this paper we corroborate that view with extensive heat-capacity measurements. We have measured the entropy of transition for many samples with different transition temperatures and have examined the transition itself in very small crystals. Furthermore, from measurements of the specific heat of stoichiometric crystals in the range 5–300 K, we have attempted to allocate the entropy among the lattice, electronic, and magnetic degrees of freedom. The result will be discussed with reference to possible transition mechanisms.

I. EXPERIMENTAL METHODS AND RESULTS

A. Sample preparation

The crystals were prepared from mixtures of the elements, 99.999% pure, in sealed evacuated quartz tubes. After an initial reaction at 500 °C, the compound was melted at 1000 °C for one week, cooled at 1 °C/h to 900 °C, annealed for several weeks, and finally quenched from 500 °C to preserve the NiAs structure which is metastable at room temperature.¹⁸ Large crystals were also prepared by the Bridgeman method, but they turned out rather inhomogeneous. The homogeneity of the slowly cooled crystals can be estimated from the width of their transition. It was typically 8 K in a 1 cm³ volume, corresponding to a 0.1% variation in nickel content.

Polycrystalline samples of differing stoichiometry, some doped with iron, were prepared by the same method, but cooled more rapidly.

B. Heat capacity and enthalpy near the transition

Most of the thermal measurements were made on a differential scanning calorimeter (Perkin Elmer

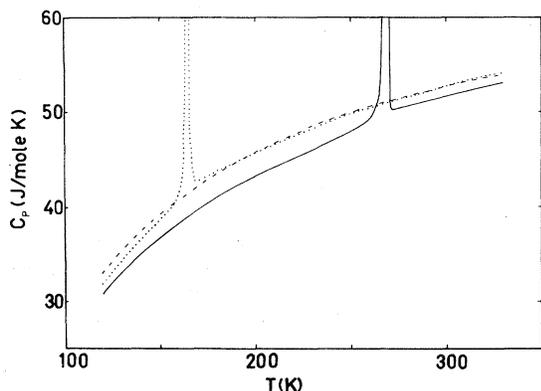


FIG. 1. Heat capacity as a function of temperature for: Solid line, $\text{Ni}_{1.00}\text{S}$; dotted line, $\text{Ni}_{0.98}\text{S}$; dashed line, $\text{Ni}_{0.95}\text{S}$. Data are obtained using 30–40-mg crystals and a heating rate of 10 K/min.

DSC-2). This instrument permits the measurement of very small samples, in the range 1–100 mg, with an absolute accuracy in the determination of the specific heat and the enthalpy change at the transition estimated as $\pm 3\%$. The sample, contained in an aluminium capsule, is mounted in the sample holder with a blank, with the reference capsule in an identical holder beside it. A constant rate of change of temperature in the range ± 0.3 –10 K/min is normally used, and the differential power which has to be supplied to follow the temperature program is recorded directly. This is the rate of energy absorption or evolution by the sample and is exactly C_p if the sample remains at all times in equilibrium. Although less accurate than adiabatic calorimetry, the technique has the great advantage that it allows the study of very small samples which come rapidly to thermal equilibrium, and details of transitions can be observed which would otherwise be lost because of the inevitable inhomogeneities in a large sample.

Benzoic acid was used to calibrate the instrument for specific-heat measurements in the range 120–330 K. The enthalpy of the transition,

$$\Delta H = \int_{T_i^-}^{T_i^+} C_p dT = T_i \Delta S,$$

was determined by direct comparison of the area of the trace with that for the melting of an indium standard. Δ is used throughout to denote the change in magnitude of some quantity at T_i .

Figure 1 shows the heat capacity of three different samples of nickel sulfide of differing stoichiometries. $\text{Ni}_{1.00}\text{S}$ has its transition at 265 K. $\text{Ni}_{0.98}\text{S}$ transits at 165 K, and $\text{Ni}_{0.95}\text{S}$ has no transition whatsoever. The width of the anomaly at half-height is at best about 2 K, and a hysteresis of 4–6 K is always observed, depending on the sample.

The data in Table I show that the step in C_p at the transition is rather small and that the enthalpy and entropy changes at the transition, ΔH and ΔS , appear to depend strongly on transition temperature. We find $\Delta S = 5.32 \pm 0.16$ J/mole K compared to the value 5.03 J/mole K reported with adiabatic calorimetry.¹⁴

A curious effect was found in very small crystals (0.5–5 mg) even if they had never previously cycled the transition. A typical result is shown in Fig. 2, where the anomaly at the transition is seen to be composed of many discrete and very sharp peaks at slightly different temperatures when a slow rate of heating or cooling is used. Each peak has a width of 0.04 K, near the limit of resolution in temperature of the calorimeter. It cannot be an instrumental effect as it was not found when other first-order transitions were studied in the same conditions. After the experiment, the small crystal was examined in a microscope. It fractured readily into even smaller crystallites with dimensions of the order of 100 μm . These observations suggest that grain boundaries or fissures open up at the transition around crystallites whose mass is of the order of 10^{-5} g. They have slightly differing transition temperatures because of slightly differing stoichiometries, but the transition in each one is very sharp indeed. It seems as if each one must be individually seeded, and they do not behave cooperatively at the transition.

The variation of ΔH with T_i mentioned above has been studied with a variety of samples of widely different nonstoichiometry (which reduces T_i) or iron content (which increases it). The results, expressed as entropy change, are summarized in Fig. 3, where the hysteresis is represented by the length of the bar. The width of the transition itself varied irregularly from 2 to 10 K. ΔS appears to be linear in transition temperature. The line drawn is $\Delta S = 1.8 \times 10^{-2} T_i$.

C. Low-temperature specific heat

The heat capacity of two large crystals, ~ 5 g, was also measured from 5 to 300 K using a differential calorimeter with power compensation.¹⁹ One crystal was almost stoichiometric, with a transition at 253 K. The other, of composition $\text{Ni}_{0.95}\text{S}$, showed no transition at all but remained metallic

TABLE I. Changes in thermodynamic parameters at the first-order transition in nickel sulfide.

Sample	T_i (K)	ΔH (J/mole)	ΔS (J/mole K)	ΔC_p (J/mole K)
$\text{Ni}_{1.00}\text{S}$	265	1409 ± 42	5.32 ± 0.16	0.8 ± 0.5
$\text{Ni}_{0.98}\text{S}$	165	454 ± 14	2.80 ± 0.09	1.0 ± 0.5
$\text{Ni}_{0.95}\text{S}$	< 4.2			

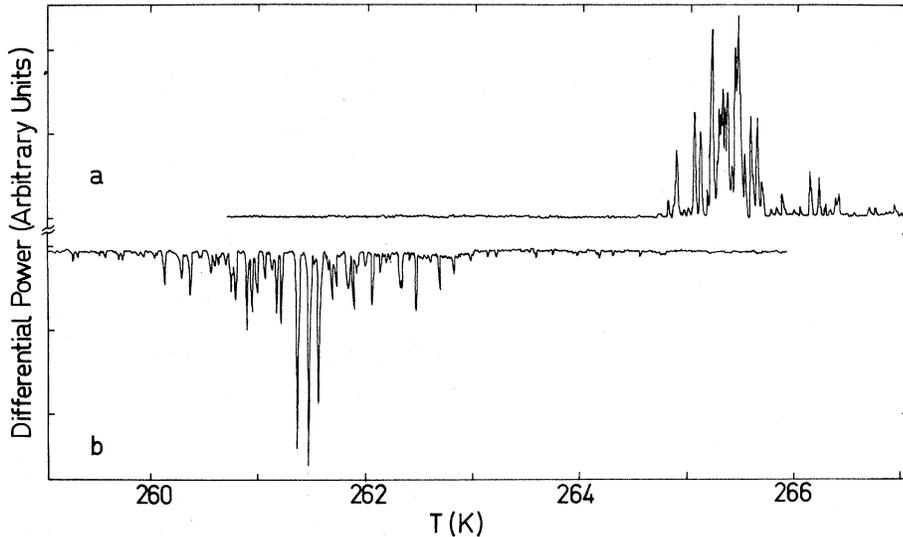


FIG. 2. Details of the transition (a) on heating and (b) on cooling a 4-mg crystal of NiS at 0.3 K/min.

down to 4.2 K.

The low-temperature data on the two crystals are shown in Fig. 4, and the best fit to the function

$$C_p = \gamma T + \beta T^3$$

was determined in each case by least squares. The parameters β and γ are listed in Table II.

II. DISCUSSION

Our measurements provide some additional evidence that the transition is first order. There is certainly hysteresis of 4–6 K in the transition temperature, and the high-resolution measurements of Fig. 2 are evidence for the seeding of small crystallites. Furthermore, the entropy change at the transition should be related to the volume change and to the pressure dependence of the transition

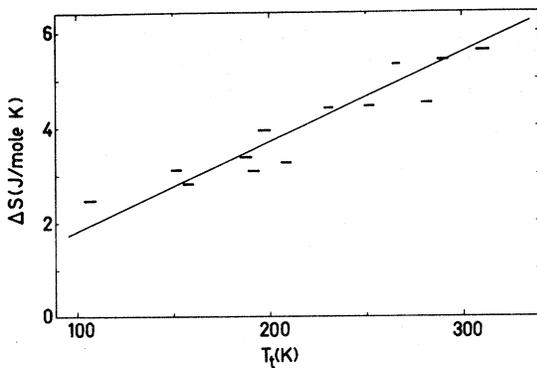


FIG. 3. Entropy of transition as a function of transition temperature for a series of nickel sulfides with different stoichiometry or iron doping. Short horizontal line, hysteresis observed for each sample; solid line, $\Delta S = 1.8 \times 10^{-2} T_t$.

temperature by the Clausius-Clapeyron equation¹²

$$\frac{dT_t}{dP} = \frac{\Delta V}{\Delta S}.$$

From the values of ΔS given in Fig. 3 we calculate $dT_t/dP = -8.3$ K/kbar at 220 K, using the volume change found in stoichiometric samples.⁶ The measured values -6.0 K/kbar⁴ and -7.5 K/kbar⁵

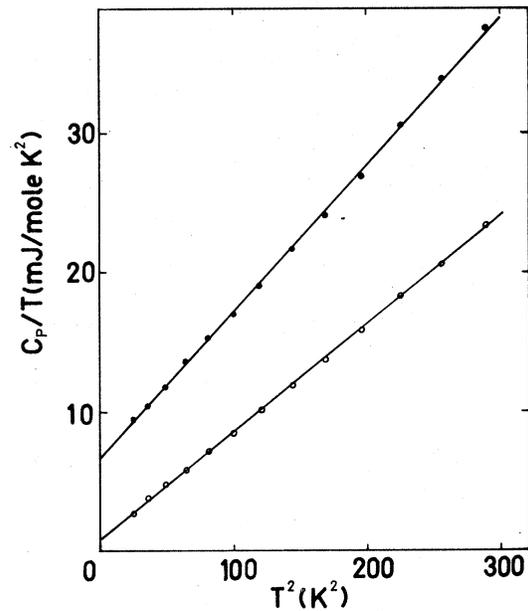


FIG. 4. Low temperature specific-heat data obtained on 5-g samples of ●, $\text{Ni}_{0.95}\text{S}$ and ○, $\text{Ni}_{1.00}\text{S}$. A heating rate of 0.5 K/min was used. Solid lines are least-squares fits to $C_p = \gamma T + \beta T^3$, and the corresponding parameters are given in Table II.

TABLE II. Low-temperature heat capacity of semi-metallic and metallic nickel sulfide.

Sample	γ (mJ/mole K ²)	β (mJ/mole K ⁴)	Θ (K)
Ni _{1.00} S	0.9 ± 0.2	0.075 ± 0.003	373 ± 5
Ni _{0.95} S	6.2 ± 0.4	0.100 ± 0.004	336 ± 5

correspond approximately to the calculated value.

Several different models for the transition have been put forward.^{10,11,15} It could be either

(a) a first-order Néel point from an antiferromagnet with ordered local moments to a paramagnet with disordered local moments;

(b) a transition from an antiferromagnet with ordered local moments to a delocalized momentless *d*-band metal;

(c) a transition from an itinerant, band antiferromagnet to a delocalized, momentless *d*-band metal.

We have recently presented a variety of magnetic evidence in favor of (c).^{16,17} Briefly, we found that the susceptibility and the temperature dependence of the sublattice magnetization in the antiferromagnetic phase are inconsistent if local moments are assumed, but may be reconciled in a simple band model. The strong dependence of the nickel moment on lattice parameter also suggested band moments. Above the transition, the spin-spin correlation time is of the order of 10⁻¹⁴ or 10⁻¹⁵ sec, as expected for a nonmagnetic *d* band. The heat-capacity and entropy measurements reported here help to clarify further the electronic nature of the two phases, and further confirm that (c) is the correct model. First, it is necessary to assign the total entropy of transition to the electronic, lattice, and magnetic degrees of freedom.

The electronic entropies of the two phases are deduced from the γT terms in the low-temperature specific heats. γ in the *metallic* phase (Ni_{0.95}S) is comparable with the values found in *d*-band metals and thus fits in with all the other evidence for metallic behavior of NiS above its transition—magnitude and temperature dependence of conductivity, susceptibility and Seebeck coefficient, short spin-spin correlation time, golden luster. The density of states at the Fermi level derived from the low-temperature specific heat (3.1 states/eV molecule) and that derived from the Pauli susceptibility, corrected for core diamagnetism (7.7 states/eV molecule) are of roughly comparable magnitude. Neither the susceptibility nor the electronic specific heat is very greatly enhanced as is the case for the metallic phases of VO₂ and V₂O₃.²⁰ If we suppose that the conduction band is simply a half-filled σ^* band formed from the nickel *e_g* and sulphur *3p* orbitals, containing two electrons per molecule, its width will be 1–2 eV, depending on its form. If

there are any enhancement effects the band would be wider.

γ is much smaller in the *antiferromagnetic* phase, but it is not zero; this shows that NiS is not a semiconductor below T_t , but a semimetal with a small density of states at the Fermi level. The change in γ at the transition can be due to a gap appearing at the Fermi surface in most directions of *k* space, as suggested by White and Mott.¹¹ The change in entropy at the transition associated with the electronic degrees of freedom is given, to first order, by

$$\Delta S_{el} = \Delta\gamma T_t = 1.40 \text{ J/mole K.}$$

This is about one-fourth of the total transition entropy, and any temperature-dependent enhancement effects in the electronic heat capacity would reduce this electronic entropy change. Consequently, the metal-semimetal transition in NiS cannot be purely electronic in nature, as was suggested by Koehler and White.²¹

The next step is to estimate the lattice contribution to the entropy of transition. This is done by again considering the low-temperature specific heats and comparing the T^3 term for the two phases. We are forced to neglect any change in the optical modes at the transition, as only the acoustic modes are excited at such low temperatures. The approximation may not be too bad, however, since there is no change in structure at T_t . Interpreted on a Debye model, the characteristic temperatures are $\Theta = 373$ and 336 K for the semimetallic and metallic phases, respectively. The lattice-entropy difference at 265 K is thence 4.75 J/mole K.

Another uncertainty exists in this estimate because we are comparing the T^3 term for stoichiometric NiS with that of Ni_{0.95}S, which has extra vacancies on the nickel sublattice²² and slightly different lattice parameters even at room temperature. The sum of the lattice and electronic contributions to the entropy of transition is thus 6.15 ± 0.90 J/mole, compared with the measured value of 5.32 ± 0.16 J/mole. The errors are the experimental errors in γ , β , and ΔS and do not take into account the uncertainties just mentioned.

The magnetic contribution to the entropy of the transition is what is left when the electronic and lattice contributions have been accounted for, that is, -0.83 ± 1.0 J/mole. In spite of the approximations made in arriving at this estimate, it seems that local moments in the metallic phase can be ruled out because the magnetic entropy would then be of order $R \ln(2S+1) \sim 8$ J/mole K, as the moments are almost completely ordered just below T_t . This corroborates the substantial evidence, mentioned above, that NiS is a normal nonmagnetic metal, above its transition and rules out model (a). At the other extreme from a localized-moment model is

the Stoner model, where the electrons, in a magnetically polarized band, are regarded as uncorrelated. Here there is no magnetic entropy in the paramagnetic state, and the change in entropy associated with the disappearance of magnetic order is purely an electronic effect due essentially to the change in density of states at the Fermi level. As such it is included in the first part of this discussion. Nevertheless, in a recent treatment of the itinerant ferromagnet, Doniach²³ has suggested that approximately 5% of the magnetic degrees of freedom may be excited in the paramagnetic phase. Regrettably, we cannot comment on the applicability of this idea to NiS because of the smallness of the entropy involved. Furthermore, antiferromagnetic and paramagnetic NiS are different phases, and there is no reason why the correlations in the metallic phase should be the same as those in the antiferromagnetic phase above its Néel point (if it had one).

We now discuss the small change in the specific heat at the transition. The step observed in C_p is 0.8 ± 0.5 J/mole K at 265 K. First the step must be corrected to one in C_v using the relation

$$C_p - C_v = -VT\beta'^2/k_T.$$

The values of the volume expansion coefficient β' and the isothermal compressibility k_T for the two phases may be derived from the data in Ref. 6 and 24. There the lattice parameters are given as functions of temperature and pressure, and $\beta' = 22 \times 10^{-6}/\text{K}$ or $36 \times 10^{-6}/\text{K}$, $k_T = -0.86 \times 10^{-12}$ or -0.73×10^{-12} cm²/dyn for the semimetallic and metallic phases, respectively. As these neutron data are not very precise, we have also measured β' with strain gauges just below and just above the transition and find values of $44.0 \times 10^{-6}/\text{K}$ and $46.4 \times 10^{-6}/\text{K}$ for the two phases. Using our values for β' , the correction $C_p - C_v$ is 1.3 ± 0.3 J/mole K just above T_t and 1.0 ± 0.3 J/mole K just below T_t , so the step in C_v at the transition is 0.5 ± 0.7 J/mole K. Once again there can be electronic, lattice, and magnetic contributions to the specific heat. The first increases by $\Delta\gamma T_t = 1.40$ J/mole K and the second by 0.80 J/mole K at the transition. It follows then that the magnetic contribution to the specific heat decreases by 2.2 ± 0.7 J/mole K at the transition, presumably because spin waves can be excited in the antiferromagnetic phase. The error is again the experimental error in the measurements and does not take account of the possibility that the electronic contribution is overestimated because of temperature-dependent correlations or that the estimate of the lattice contribution takes no account of a possible change in the optical modes at the transition. If model (b) were correct, insulator spin-wave theory could be applied and the magnetic specific heat C_{mag} would be given approxi-

mately by

$$C_{\text{mag}} = cR kT^3/2zJS,$$

where C is a constant of order 10. The exchange constant is taken from the inelastic neutron data of Ref. 25, and the calculated magnetic specific heat just below the transition is only 0.02 J/mole K. We already found that the exchange constants deduced from the spin-wave dispersion relation using insulator spin-wave theory were much too high compared with those derived from the extrapolated Néel temperature,⁸ and that the inconsistency could be resolved in a band model for the magnetism and antiferromagnetic NiS.¹⁷ The disagreement between the observed magnetic specific heat just below the transition and its value calculated on the local-moment model also suggest that model (b) is not the correct description of the transition. Model (c) wins by default, as we have at present no theory of the magnetic excitations in an itinerant antiferromagnet with which to compare our result. It may be noted that if the observed C_{mag} is proportional to T^3 , the coefficient 0.1×10^{-6} J/mole K⁴ is negligible compared with the measured lattice T^3 term.

The proportionality between entropy of transition and transition temperature (Fig. 3) is an interesting result and may be compared with the linear relation between the change in thermoelectric power and transition temperature found by Townsend *et al.*¹² (the Seebeck coefficient contains a term equal to the entropy associated with the carriers). If the entropy of transition was purely the electronic $\Delta\gamma T_t$ term, then ΔS would be proportional to T_t . However, we have shown that most of the entropy of transition is associated with the lattice, so the proportionality suggests that the electron-phonon interaction may be important in the metallic phase. Another indication that the electron-phonon interaction in the metallic phase does play a role in the transition is simply provided by the sign of the volume change. According to the Grüneisen relation

$$\gamma_g = \frac{-\Delta\Theta}{\Theta} \frac{V}{\Delta V} = \frac{-\beta'V}{K_T C_v}.$$

γ_g is evaluated as 2.2 from the right-hand side in the metallic phase. The change in Debye temperature at the transition, $\Delta\Theta = -37$ K, implies a volume *increase* of 4.5%. The observed volume change is a *decrease* of 1.9%, which is possible if the interatomic Coulomb interactions are screened by the conduction electrons in the metallic phase.

Finally, we comment on possible mechanisms for the transition. The Shimizu development of the Stoner model²⁶ is capable of reproducing the first-order disappearance of band magnetism found in NiS in a phenomenological way, provided a suitable

form is chosen for the $3d$ conduction band. The essential requirement is that there should be a minimum in the density of states at the Fermi level, and susceptibility measurements indicate that this is probably so.^{15,17} In such a case, itinerant magnetism can appear without the Stoner condition being satisfied, but it will disappear at a first-order transition. The trouble with this, and any other purely electronic model, is that the calculated entropy of the transition is only a fraction of the observed value.

Other effects which can give rise to a first-order transition are a decrease in exchange interaction or an increase in bandwidth as a function of temperature. The recent band-structure calculation of Kasowski, which included a Debye-Waller factor,²⁷ has shown that the bandwidth and p - d overlap are rather temperature dependent because of the lattice vibrations. The Mott-Hubbard state disappears in this model when the ratio of bandwidth W to intra-atomic Coulomb interaction U exceeds some critical value. The critical value of W/U can also be attained if U decreases with temperature. A possible reason for this is linked to the magnetic order. In the ordered state White and Mott¹¹ have suggested that the Mott-Hubbard gap appears in the c direction, but not in the c plane. The electrons are thus quite delocalized in the planes which are ferromagnetic, but can move parallel to c only by activation or tunneling. As the temperature increases the moment falls by up to 10%, and the area of the Fermi surface around the c axis with a gap diminishes. The electrons

can thus become increasingly delocalized in directions which do not lie in the plane, and there will be a consequent reduction of U because of greater screening of the intra-atomic Coulomb interaction. In other words the disappearance of magnetism could be an effect of electron delocalization by magnetic disorder, and a magnetic origin for the transition remains a possibility.

III. CONCLUSIONS

Nickel sulfide is a compound in which the conditions for the appearance of magnetism are barely satisfied. It changes from a semimetallic itinerant antiferromagnet without local moments into a normal nonmagnetic metal at a first-order transition. Domain effects appear even in very small crystals. The origin of the increase in entropy at the transition is only about one-fourth in the electrons and three-fourths in the lattice. Any magnetic contribution to the entropy of transition is much less than $R \ln(2S+1)$. It is possible, however, that there is a substantial magnetic contribution to the specific heat in the antiferromagnetic phase, just below the transition.

The results eliminate any model of the transition which considers only the electrons, and suggest that the electron-phonon interaction must be taken into account.

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