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Thermodynamics of the semiconductor-metal transition in Ni_{1-x}S

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A calorimetric study was made of the semiconductor-metal phase transition in Ni_{1-x}S samples with different critical temperatures (160-265°K). The contribution of the electron, spin, and phonon degrees of freedom to the change in the thermodynamic properties of the system was determined. Some of the concomitant phenomena—the dependence of the kinetics of the transition on the crystal size, discrete nature of the thermal effects in bulk crystals, and the fracture of the latter as a result of multiple crossing of the transition point—were attributed to the influence of stresses created by the structural transition accompanied by a change in the specific volume.

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Nickel sulfide (NiS) with the hexagonal NiAs-type lattice is an example of a substance in which the insulator-metal (IM) phase transition occurs, with rising temperature, due to a simultaneous change in the electronic and magnetic subsystems of a crystal.^[1-7] At low temperatures, NiS is a semiconducting antiferromagnet with a magnetic moment, per nickel atom, close to two Bohr magnetons ($\sim 1.7 \mu_B$). At a first-order transition point, $T_c \sim 265^\circ\text{K}$, the magnetic order disappears suddenly (the sublattice moment falls from a value approximately equal to 0.9 of the maximum moment) and, at the same time, the substance becomes a metal. The conductivity increases abruptly by about two orders of magnitude, which corresponds to the collapse of an energy gap of $\sim 0.2 \text{ eV}$.^[8] Above T_c , there is no magnetic diffuse neutron scattering (the magnetic moment is $\sim 0.5 \mu_B$) and the high-temperature phase exhibits properties of a *d*-band Pauli paramagnet. The transition is accompanied by a change in the sign of the carriers from positive to negative,^[3,4] and by abrupt changes in the magnetic susceptibility^[2,5] and lattice parameters^[1,9,10]; the specific volume and the axial ratio *c/a* decrease correspondingly by 1.9 and 1%. The symmetry of the NiS lattice is not affected by the IM transition.^[9] The temperature of the electronic transition in Ni_{1-x}S depends strongly on the composition, decreasing with deviation from stoichiometry, and it vanishes at $x = 0.03-0.04$.^[1,6,7] The fall of T_c is accompanied by a reduction in the conductivity jump.^[7]

An agreed interpretation of the properties of the

Ni_{1-x}S system has not yet been worked out. In particular, the thermodynamic stimulus and the nature of the IM transition in this system at finite temperatures remains unresolved. The present paper reports a calorimetric investigation of the IM transition in Ni_{1-x}S samples with controlled compositions (with different values of T_c). We shall separate the contributions of the various degrees of freedom to the change in the thermodynamic properties of the system.

METHOD AND EXPERIMENTAL RESULTS

The compositions and morphology of the investigated samples are given in Table 1. Polycrystalline samples (sintered aggregates and powders) were synthesized from very pure components by the usual method.^[7] Single crystals were prepared by crystallization from the melt at a rate of 3.6 mm/h in a furnace with a temperature gradient of 70 deg/cm. The NiAs-type structure was frozen by quenching from 400°C in water. The quality of the single crystals was determined by x-ray diffraction. A local x-ray spectroscopic analysis, carried out using a JXA-5 microprobe, indicated that the inhomogeneity of the distribution of the components did not exceed $\pm 1 \text{ rel.}\%$. The specific heat and thermal effects associated with the IM transition were determined with a recording microcalorimeter of sensitivity down to $1 \times 10^{-7} \text{ W}$.^[11] The advantage of this method was the ability to determine (with an error not exceeding 6%) the properties of small samples (1-100 mg) in which the composition and structure inhomogeneities

TABLE 1. Thermodynamic characteristics of IM transition in Ni_{1-x}S .

Composition	Morphology	Thermal hys- teresis, deg	Phase "equi- librium" tem- perature, °K	ΔH , J/mole	ΔS , $\text{J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$
$x = 0 \pm 0.003$	Powder	7.3	267.4 ± 0.2	1390 ± 40	5.20 ± 0.15
$x = 0.007 \pm 0.003$	Powder	4.0	217.5 ± 0.2	960 ± 30	4.40 ± 0.12
$x = 0.013 \pm 0.003$	Powder	4.1	165.8 ± 0.2	480 ± 20	2.90 ± 0.12
$x = 0.007 \pm 0.003$	Sintered polycrystal	4.0	220.5 ± 0.5	980 ± 50	4.50 ± 0.30
$x = 0.010 \pm 0.003$	Single crystal	5.0	190.5 ± 1.0	655 ± 30	3.50 ± 0.20

due to the separation technology were reduced to a minimum. At the rates of change of temperature employed (~ 5 deg/h), these samples were very close to the state of thermal equilibrium; the temperature drop between the surface and the center of a sample, representing the "nonisothermicity" under the experimental conditions, did not exceed 0.01 deg.

The results of measurements of the specific heat of four samples in the immediate vicinity of the phase transition are plotted in Fig. 1, where curve 1 represents an almost stoichiometric powder, curve 2 a powder with a cation concentration $x = 0.007$, curve 3 a sintered polycrystalline sample of the same composition and with 1–3 mm grains, and curve 4 a $2 \times 2 \times 3$ mm single crystal ($x = 0.01$). The particle size in the powders ranged from 0.05 to 0.4 mm. All the curves in Fig. 1 were obtained by cooling at a rate of 5 deg/h. The specific heat anomalies of the single crystal and sintered coarse-grained polycrystalline sample had a "fine structure" in the form of a multitude of sharp peaks, whose smallest amplitude was close to the resolution limit of the calorimeter.

It is clear from Fig. 1 that the specific heat jump at the transition was very small. According to our data, it did not exceed $\pm 1.0 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$. The adiabatic calorimetry was used in^[12] to investigate a stoichiometric sample and the jump $\Delta C = C_M - C_I$ was estimated to be $0.6 \pm 0.5 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$. In estimating the changes in the enthalpy ΔH and entropy ΔS , the normal part of the specific heat was found by extrapolation of the measured values of C from high and low temperatures. The values of ΔH and ΔS found in this way are included in Table 1. This table also gives the thermal hysteresis observed during cooling and heating and the phase "equilibrium" temperature $T_c = \frac{1}{2}(T_{\text{cool}} + T_{\text{heat}})$. Clearly, the values of ΔH and ΔS decrease with increasing concentration of cation vacancies x and with decreasing critical temperature.

The dependence of the transition entropy on the critical temperature of Ni_{1-x}S samples of different compositions was plotted in Fig. 2 on the basis of our results and those reported in^[12] for a stoichiometric polycrystalline sample and in^[5] for two single crystals with $T_c = 267$ and 228 °K. The dependence was found to be nearly linear. In preparing the manuscript for press, we had an opportunity to become acquainted with the results of a similar investigation carried out by Coey and Brusetti.^[13] The values of $\Delta S(T_c)$ and of the transition hysteresis reported in^[13] are represented in

Fig. 2 by horizontal lines of suitable width. It is clear that, in spite of the different methods used in the preparation and investigation of the samples,^[1] the two sets of results were in good agreement. It was reported in^[13] that the jump in the specific heat at the first-order phase transition point did not exceed $1.0 \pm 0.5 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$.

Coey and Brusetti observed a discrete structure of the thermal effects in small NiS crystals (~ 5 mg), which was similar to that observed by us for fairly large single crystals and coarse-grained polycrystalline samples. They attributed this structure to composition fluctuations as a result of which the abrupt first-order transition occurred at similar but not identical temperatures in parts of a ~ 0.1 mm sample. We would not exclude this as one of the possible explanations but we regard it as more probable that the discrete structure is a manifestation of a disordered relaxation of intrinsic elastic stresses resulting from changes in the crystal structure. In the case of a homogeneous distribution of a new (compressed) phase in an elastically isotropic matrix, the variance of the structure of stresses which appear solely because of a change in the specific volume can be estimated from^[14]

$$D_\sigma \approx 18.5 e^2 f(1-f) E^2, \quad (1)$$

where e is the volume effect of the phase transition, f is the relative content of the new phase, E is the average Young modulus of both phases. The formula (1) is valid on condition that f is close to unity or to zero

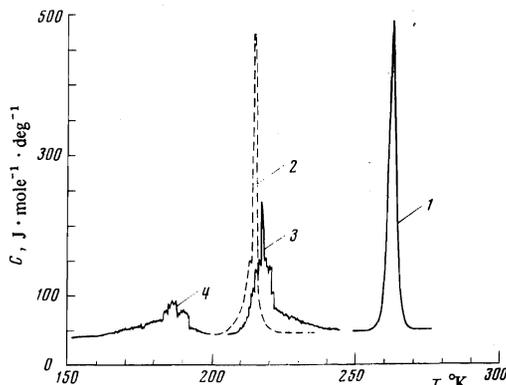


FIG. 1. Specific heat of four samples of Ni_{1-x}S near the IM transition: 1) near-stoichiometric powder; 2) powder with $x = 0.007$; 3) sintered polycrystalline sample $x = 0.007$; 4) single crystal with $x = 0.010$.

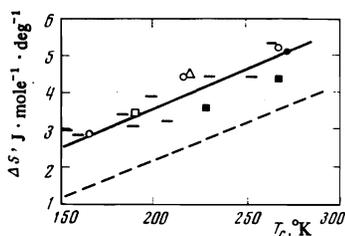


FIG. 2. Change in the entropy at the IM transition plotted as a function of T_c of Ni_{1-x}S samples of different composition: ○) our results for powders; □) our results for a single crystal; △) our results for a sintered polycrystalline sample; ●) powder, results from^[12]; ■) single crystals, results from^[5]. The horizontal bars represent the values of ΔS and the hysteresis of the transition for polycrystalline samples investigated in^[13]. The continuous line is the dependence $S(T_c)$ calculated on the assumption that $g_m = 2.4$ and the dashed line is the dependence calculated for $g_m = 2.0$.

(there are no stresses if $f = 0$ or $f = 1$) and the medium remains continuous.

The Poisson ratio is assumed to be $1/3$. In this case, the Young modulus E is numerically equal to the bulk modulus. Assuming for NiS the values $\nu = 0.019$ ^[1, 9, 10] and $E \approx 1.3 \times 10^3$ kbar,^[10] we find that, if $f = 0.1$, the standard deviation of normal stresses from the average (zero) value is $d_\sigma = (D_\sigma)^{1/2} \approx E/40 \approx 30$ kbar. An estimate shows that intrinsic stresses which appear in NiS crystals as a result of a phase transition may be very considerable and even comparable with theoretical tensile strength.²⁾ The relaxation processes reduce the actual local-equilibrium elastic stresses in an NiS crystal (deduced from the broadening of the transition) to a value not exceeding ± 3 kbar ($dT_c/dP \sim -6$ deg/kbar^[9, 10]).

Several experimental investigations demonstrated that an important mechanism in the relaxation of structural stresses in NiS crystals is the formation of discontinuities at the boundaries of a new phase.

1. An x-ray diffraction investigation of single crystals failed to establish a regular correspondence between the lattices of the initial and final phases during all stages of the transition; moreover, there were no manifestations of the accommodation of stresses by twinning or domain formation.

2. The results of a granulometric analysis of an almost-stoichiometric NiS powder (Table 2) indicated that the number of larger particles decreased considerably after several IM transition cycles. Particles of ~ 0.1 mm in size, corresponding to the center of gravity of the size distribution, were clearly close to the maximum volume in which each of the phases could exist irrespective of what happened in neighboring parts of the system. The size of such "single-domain" particles in NiS was clearly limited by the mechanical properties of the substance. Experiments carried out on sieved powders of the same composition (Fig. 3) indicated that, when particles were nearly single-domain in size (< 0.06 mm), the phase transition broadening was considerably less than for powders of larger particles. The integrated thermal effect and the transi-

TABLE 2. Distribution of particles in Ni_{1-x}S powder ($x = 0 \pm 0.003$).

Particle size, mm	Content, wt. %	
	Before transition	After 5 transition cycles
< 0.05	4.0	4.0
0.05 - 0.1	20.0	31.0
0.1 - 0.2	34.0	42.0
0.2 - 0.3	28.5	21.0
0.3 - 0.4	13.5	2.0

tion point were not affected.

3. Experiments on single crystals revealed a dependence of the integrated thermal effect of the phase transition on the number of cooling-heating cycles across the critical point. After five cycles, ΔH of a single crystal ($x \approx 0.01$) increased from 530 to 655 ± 30 J/mole and then ceased to vary. After repeated passage through the transition point, the single crystals broke up into smaller crystallites of 0.1 mm in size. Fracture made it difficult to investigate the electrical properties of NiS single crystals near the phase transition point.

DISCUSSION OF RESULTS

We shall use the published information in determining the contributions of the electron, spin, and phonon degrees of freedom to the changes in the thermodynamic properties of Ni_{1-x}S at the IM transition. The low-temperature specific heat of stoichiometric nickel sulfide and of a sample of $\text{Ni}_{0.95}\text{S}$ which remained a metal down to 0 °K was investigated by Ohtani *et al.*^[16] and by Coey and Brusetti.^[13] Using, after Ohtani *et al.*,^[16] the coefficients of the electronic specific heat of the metallic "insulating" phases $\gamma^m = 12$ and $\gamma^i = 5.2$ mJ · mole⁻¹ · deg⁻², we find that the contribution of the collective-state electrons to the change in the entropy and specific heat of NiS at the IM transition is $\Delta S_{ce} = \Delta C_{ce} = 1.8 \pm 0.1$ J/mole. Thus, the change in the entropy which can be attributed to conduction electrons represents only 0.3 of the total change in the entropy found experimentally for stoichiometric samples (5.20 ± 0.15 J · mole⁻¹ · deg⁻¹). This is in conflict with the idea that the IM transition in NiS is a purely electronic process due to a change in the density of states at the Fermi level.^[5] A similar conclusion was reached by Coey and Brusetti on the basis of their values $\gamma^i = 0.9$

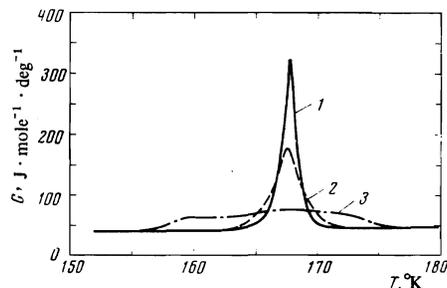


FIG. 3. Specific heat of a sieved powder with $x = 0.013$ and grain size (mm): 1) 0.05; 2) 0.07-0.09; 3) 0.10-0.15.

and $\gamma^m = 6.2 \text{ mJ} \cdot \text{mole}^{-1} \cdot \text{deg}^{-2}$.

The symmetry of the NiS lattice is not affected by the IM transition and, therefore, the contribution of the lattice to the entropy and specific heat jumps, ΔS_L and ΔC_L , can be estimated using the Debye approximation and ignoring the contribution of the optical phonon branch. The Debye temperatures of the two phases^[13,16] differ in respect of the absolute value and of the ratio Θ^m/Θ^i : $\Theta^i = 157.2 \text{ }^\circ\text{K}$ and $\Theta^m = 164 \text{ }^\circ\text{K}$ ^[16]; $\Theta^i = 375 \text{ }^\circ\text{K}$ and $\Theta^m = 336 \text{ }^\circ\text{K}$.^[13] This very large difference between the two sources makes it highly desirable to carry out control experiments. However, there are several reasons why preference should be given to the results of Ohtani *et al.*^[16]

1. The T^3 Debye law gives a correct Θ only in the range of temperatures several degrees higher than $T = 0$ (the Debye specific heat expressed as the dependence of C/T on T^2 has a maximum at $T^2/\Theta^2 \sim 7.5 \times 10^{-2}$). This condition is largely satisfied in the experiments of Ohtani *et al.*,^[16] in which the specific heat was measured at fairly low temperatures of $1.5\text{--}7 \text{ }^\circ\text{K}$ ($T^2/\Theta^2 = 8.4 \times 10^{-5}\text{--}1.8 \times 10^{-3}$). The corresponding measurements in^[13] were carried out at higher temperatures: $5\text{--}17 \text{ }^\circ\text{K}$ ($T^2/\Theta^2 = 1.8 \times 10^{-3}\text{--}1.0 \times 10^{-2}$) and, in this case, the value of Θ could be overestimated.

2. The adiabatic calorimetry method used in^[16] is more accurate than the method of continuous heating at a rate of 30 deg/h employed by Coey and Brusetti.^[13]

If we use tables of the Debye functions^[17] for $\Theta^i = 157.2 \text{ }^\circ\text{K}$ and $\Theta^m = 164 \text{ }^\circ\text{K}$, we find that, at $T_c = 265 \text{ }^\circ\text{K}$, the changes are $\Delta S_L = -2.10 \pm 0.30 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$ and $\Delta C_L = -0.15 \pm 0.10 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$. In comparing the contributions of the lattice and conduction electrons with the experimental data, we must allow also for the values of C_a and S_a due to the anharmonicity effects:

$$C_a = C_p - C_v = \frac{\beta^2 VT}{\alpha_T}, \quad S_a = \int_0^T \frac{\beta^2 V}{\alpha_T} dT.$$

Using the compressibilities $\alpha_T^i = 8.6 \times 10^{-4} \text{ kbar}^{-1}$ and $\alpha_T^m = 7.3 \times 10^{-4} \text{ kbar}^{-1}$ ^[10] and the thermal expansion coefficients $\beta^i = 2.2 \times 10^{-5} \text{ deg}^{-1}$ and $\beta^m = 3.6 \times 10^{-5} \text{ deg}^{-1}$,^[11,10] we obtain $\Delta C_a = \Delta S_a = 0.50 \pm 0.30 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$. The combined contribution of the lattice and conduction electrons, including corrections for their anharmonicity, gives the specific heat and entropy jumps $\Delta C' = 2.15 \pm 0.35 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$ and $\Delta S' = 0.20 \pm 0.45 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$, which are quite different from the experimental values.

Phenomenological models of the IM transition in an antiferromagnet which allow for the influence of the magnetic order on the excitation of localized d electrons in the conduction band were put forward by Falicov *et al.*^[18] and Alascio *et al.*^[19] The model of Alascio *et al.*^[19] allows for the contribution to the change in the entropy due to partial disordering of the magnetic moments,

$$\Delta S_m = k p_c \left(\int_0^{m_c} B_s^{-1}(m) dm - \ln g_i \right), \quad (2)$$

and for the configurational and paramagnetic contributions of localized d electrons,

$$\Delta S_{i,c} = k p_c \left[\ln g_m + \ln p_c + \left(\frac{1-p_c}{p_c} \right) \ln(1-p_c) \right], \quad (3)$$

where k is the Boltzmann constant, p_c is the relative concentration of localized electrons at the transition point (it is assumed that each cation gives up not more than one electron to the conduction band); m_c is the relative jump in the magnetization; g_i is the multiplicity of the ground atomic state $3d^6$; g_m is the multiplicity of the atomic state with a hole; B_s^{-1} is the reciprocal Brillouin function for the spin $S=1$. Following the experimental results,^[16] we shall assume that the carrier mobility in NiS does not change greatly at the IM transition point and the jump in the electrical conductivity is solely due to a change in the concentration of current excitations $\sigma_m/\sigma_i = 1/(1-p_c)$. Using the experimental values $m_c = 0.9$ ^[11] and $\sigma_m/\sigma_i \approx 6 \times 10^2$,^[7] we find that, in the case of stoichiometric NiS, the change in the entropy is $\Delta S_m = -2.60 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$.

No definite information is available on the degree of degeneracy of the d shell of the cations in NiS after excitation of carriers.³⁾ In a sufficiently strong crystal field, both excited states of a cation—one with an electron missing from the e shell and the other with an excess electron in this shell—represented by the configurations $(t_2^6)e$ and $(t_2^5)e^3$ in the valence states Ni^{3+} and Ni^+ —are characterized by multiplicity factors close to the pure spin factor ($g_m = 2$).^[20] The corrections associated with the influence of the crystal field, spin-orbit coupling, and hybridization of localized and band states (which generally depend on temperature) may result in a deviation of g_m from the pure spin value. The best agreement with the experimental results is given if we assume that the degree of degeneracy is $g_m = 2.4$. When this value is used, we find that, in the case of NiS, we have $\Delta S_{i,c} = 7.3 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$. Hence, the total change in the entropy at the transition point is estimated to be $\Delta S = \Delta S' + \Delta S_m + \Delta S_{i,c} = 4.9 \pm 0.5 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$ (the experimental value is $5.20 \pm 0.15 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$).

The excess specific heat of the conducting phase, associated with the magnetic disorder and excitation of electrons from localized states, ensures a negative jump in the specific heat of $-2.0 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$ at the transition point. Hence, allowing for the contributions discussed above, we find that the total change is $\Delta C = 0.15 \pm 0.5 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$, which is in good agreement with the experimental results. A self-consistent equation for the magnetization [Eq. (4.3) in^[19]] gives $T_N^0 \approx 475 \text{ }^\circ\text{K}$ for the temperature of disordering of the magnetic moments or the Néel point of stoichiometric NiS; this value is in satisfactory agreement with estimates obtained from Mössbauer measurements (400–465 $^\circ\text{K}$).^[21,22]

The dependence of the entropy of the IM transition in the Ni_{1-x}S system on the transition temperature, calculated using the above values of T_N^0 , g_i , and g_m , is the continuous curve in Fig. 2. In plotting the dependence $\Delta S(T_c)$, we assumed that the temperature-dependent

contributions of the lattice conduction electrons to the entropies of the phases do not differ from the corresponding contributions in the case of the stoichiometric sulfide. In accordance with the experimental results,^[7] it was assumed that, in nonstoichiometric Ni_{1-x}S, the formation of a vacancy in the cation sublattice is accompanied by the formation of two acceptor levels with an excess positive charge (Ni³⁺) ensuring *p*-type conduction in the *p* band even at relatively low temperatures because only 1 - 3*x* of the host cations participate in the excitation of intrinsic carriers. An estimate of *p_c* from the experimentally determined conductivity jumps in Ni_{1-x}S samples of controlled composition^[7] was obtained in the same approximation that was applied to the stoichiometric sulfide. The dashed curve in Fig. 2 is the dependence *S*(*T_c*) expected in the case of the pure spin value of the degree of degeneracy (multiplicity factor) *g_m* = 2. Using the Debye temperatures $\Theta^i = 375^\circ\text{K}$ and $\Theta^m = 336^\circ\text{K}$, which gave $\Delta S_L = 4.75 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$ and $\Delta C_L = 0.80 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$, Coey and Brusetti^[13] concluded that the acoustic lattice vibrations dominated the process of stabilization of the NiS phase. They compared the experimental results with the contributions of the lattice and conduction electrons and estimated the "magnetic" components of the specific heat and entropy jumps $\Delta C_M = -2.2 \pm 0.7 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$ and $\Delta S_M = -0.83 \pm 1.0 \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$, but they were unable to explain these values quantitatively. Coey and Brusetti attributed the antiferromagnetism of the low-temperature phase to conduction electrons; they rejected the intraatomic correlation and localized magnetic moments in this phase. This point of view is in conflict with the majority of existing models of the IM transition in NiS^[23-25] in which the "insulating" phase is assumed to contain, in some way, localized antiferromagnetically ordered magnetic moments. The presence of localized *d*-electron spins in the low-temperature phase of NiS is supported by the above analysis of the results on the thermodynamics of the transition.

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¹⁾The method of differential scanning calorimetry with high rates of temperature variation (up to 600 deg/h) was used in^[13].

²⁾It should be noted that, although the theoretical stresses needed to break atomic bonds amount to *E*/5, brittle sub-

stances usually fracture at stresses of just $\sim E/500$.^[1b]
³⁾The nature of the intrinsic conduction of the low-temperature phase of NiS has not yet been determined.

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