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Heat Capacity of Hexagonal NiS: Metal-Nonmetal Transition[*]

Jeffrey Trahan and R. G. Goodrich

Department of Physics and Astronomy, Louisiana State University,
Baton Rouge, Louisiana 70803

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The heat capacity of hexagonal NiS has been measured from 35 to 330 °K. Changes in enthalpy and entropy across the metal-nonmetal transition were found to be 1383 J/mole and 5.03 J/mole deg, respectively. Measurements near the critical temperature have been made in extreme detail.

I. INTRODUCTION

A large amount of interest has recently been shown in trying to explain the metal-nonmetal (MNM) phase transition which occurs in some solids. Although this type of transition was originally proposed by Mott in 1949,[1] there are experimental and theoretical reasons for a revival of work directed toward explaining the phenomena. Experimental advances in material preparation have led to new measurements on relatively pure samples and it has been found that quite a large number of compounds exhibit the MNM transition. It is now known that the MNM transition should not be considered a rare and exceptional case, but rather a frequently observed phenomenon which demands an adequate explanation. Theoretically, the MNM transition remains a challenging and largely unsolved problem. One-electron theory is simply inadequate to explain it, and the transition is one of the more striking many-body effects in solid-state physics. At present the many-body theory of this transition is highly speculative at best and consists largely of proposed "mechanisms" which drive the transition rather than fundamental calculations.

Of critical importance to a theory of the MNM transition is the manner in which it predicts the thermodynamic behavior of a solid at this transition. That is, is the transition of first or second order, what is the entropy and enthalpy change at the transition, and what is the temperature dependence of the thermodynamic functions near the transition? This paper reports the results of measurements of the specific heat near the MNM transition in NiS. In addition, values of the entropy and enthalpy changes at the transition are given and some comments are made about the thermodynamic order of the transition.

Stoichiometric NiS crystallizes in two structures, a rhombohedral phase (millerite)[2] and a hexagonal phase (NiAs).[3] Although the rhombohedral phase is the stable phase at room temperature, the hexagonal phase can be made to exist stably at room temperature by quenching it from above 652 °K. This hexagonal phase exhibits a sharp MNM transition near 270 °K.[4] In addition, neutron diffraction studies have shown that the material becomes antiferromagnetically ordered at this same temperature.[5] Below the transition temperature, the magnetic structure is found to be a simple two-sublattice structure in which the magnetic moments of the Ni atoms are coupled ferromagnetically within {001} planes and antiferromagnetically between adjacent {001} planes. This results in the magnetic unit cell being identical to the chemical unit cell. Furthermore, it is found that the sublattice magnetization is within 10% of saturation upon ordering. There is apparently little or no magnetic moment associated with the Ni atoms above the transition in the metallic state.

In addition to the powder neutron diffraction

studies of Sparks and Komoto,[4,5] measurements of the magnetic susceptibility and electrical resistivity through the transition have been made by the same authors.[6,7] These measurements along with the neutron diffraction data indicate that the transition is of first order, exhibiting considerable hysteresis and a volume change. The c/a ratio is observed to increase on cooling through the transition with the a and c lattice parameters increasing by 0.3 and 1%, respectively.[7] A recent x-ray diffraction investigation[8] has shown that there is possibly a slight crystal distortion at the transition with the symmetry of the unit cell changing from $P6_3/mmc$ in the metallic phase to $P6_3mc$ in the nonmetallic phase.

II. EXPERIMENT

The NiS samples used in this experiment were prepared in a manner similar to that described in Ref. 8. High-purity Ni powder (quoted purity 99.999%) purchased from Johnson, Matthey, and Company was first reduced in a hydrogen atmosphere at 500 °C for several hours. After the reduction process the Ni powder and an equal atomic percent of sulphur (quoted purity 99.999%), purchased from American Smelting and Refining Company, were sealed in an evacuated quartz tube. The Ni and S were reacted at 110 °C, then melted, and after melting left at 900 °C for one week. The temperature of the resulting ingots was then reduced to 650 °C in 50° steps over a period of approximately three weeks. After this annealing, the temperature was reduced over a period of several days to 400 °C, at which time the ingot was quenched by dropping it from the furnace into room-temperature water. The portions of the ingot which were at the 50 at.% Ni concentration were selected by cooling the ingot to −10 °C at which point the stoichiometric composition undergoes the MNM transition and breaks away from the nonstoichiometric parts. The pieces selected in this manner were then powdered and pressed into cylindrical pellets approximately 13 mm in diameter and 13 mm long. A pellet of this size weighs about 8 g. The pellets were again placed in evacuated quartz tubes and sintered at 725 °C for three days, after which the temperature was slowly lowered to 400 °C before quenching in cold water. Different samples prepared in this manner all show approximately the same transition temperature and width of the transition. This procedure differs from that described previously in Ref. 8 and the sharpness of the transition shows that the final samples obtained by the present procedure are of more uniform stoichiometry than has been previously obtained.

The specific-heat measurements were performed in an adiabatic vacuum calorimeter of conventional design. The sample was suspended by a nylon thread from the top of a vacuum-tight radiation shield which in turn was suspended from the top of the cryogenic system by a thin-wall stainless-steel tube (~ 90 cm long). This entire assembly was sealed inside of a second vacuum jacket which was immersed in one of liquid helium, liquid nitrogen, or dry ice and alcohol baths. The temperature of the radiation shield relative to the sample temperature was regulated with a differential thermocouple in conjunction with a proportional temperature controller which regulated a heater wound on the radiation shield. A second small heater was wound on an aluminum form and glued with high-thermal-conductivity varnish into a hole which had been spark eroded along the axis of the cylindrical sample. An additional thermocouple was attached to the sample in order to measure its absolute temperature. Since NiS often cracks upon passing through the MNM transition, the samples were encapsulated in gold leaf (glued on) to assure that the radiation from the surface would be from a constant surface condition. The mass of all of the addenda in thermal contact with the samples was less than 1% of the mass of the samples themselves.

The thermocouple used to measure the sample temperature was connected to a six-dial potentiometer (Rubicon model No. 2768, 0.1-μV resolution) which was used to offset the major portion of the thermocouple voltage. The off-balance voltage was amplified with a Kiethley 147-nV null detector and recorded continuously on a strip-chart recorder. The over-all noise level of the measuring system was 0.01-μV short-term (~ 1 sec) and 0.05-μV long-term drift. This corresponds to a temperature resolution for the copper-constantan thermocouple used of 0.25-mK short-term and 1.25-mK long-term drift in the neighborhood of the transition. The entire system calibration was checked by measuring the specific heat of pure copper over the range of temperature near the transition. The measured values were within 1% of the published values.[9] The thermocouples were referenced to the melting point of H_2O and were calibrated at several standard-reference-point temperatures.

Continuous heating curves were recorded and used to compute the specific heat from 35 to 330 °K. Data were obtained from two different samples. The heater imbedded in the sample was used to heat the sample with a known amount of power and the radiation shield was maintained at the same temperature as the sample. The specific heat on the heating run was calculated in the conventional manner.

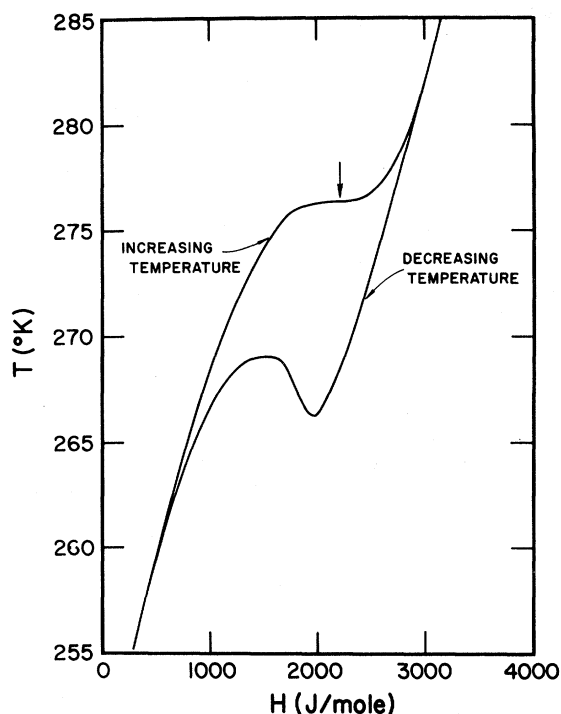Only in the neighborhood of the specific-heat anomaly were continuous measurements of the

FIG. 1. Enthalpy vs temperature of NiS, sample No. 1. The zero level of the enthalpy has been arbitrarily chosen. The arrow indicates the point of minimum slope on enthalpy curve.

specific heat made while cooling the sample. This was done by maintaining the radiation shield at a lower measured temperature than the sample, thus extracting heat from the sample by radiation exchange. The temperature difference between the sample and shield were usually on the order of 1 °K. The difference in the end-point temperatures over which the cooling run was made was 18 °K. Measurements of the specific heat at the end-point temperatures were made in the conventional manner for calibration purposes. Since the power necessary to give the correct value of the specific heat at the end-point temperatures is known, an extrapolation of the power can be made between these points. Provided the temperature difference in the end-point temperatures is relatively small, a linear extrapolation of the power can be made. In this temperature range, with an end-point temperature difference of 18 °K, T^4 differs from linearity by a maximum of 0.75%. This is probably a good estimate of the maximum error introduced in the power by making a linear extrapolation of the power across the range of temperature over which the cooling run was made.

Since preliminary measurements had indicated that the equilibrium times for NiS near the MNM transition are extremely long, several heating and

cooling rates were used to check for nonequilibrium effects. A run was performed in which both the heating and cooling rates were at the limits of stability for the calorimeter and three weeks were required to heat or cool the sample over a 10° range near the transition. These results did not differ within experimental error from those obtained when the heat input or output was adjusted to cover the same temperature range in 36 h. Faster rates, of order 1 h for the same temperature range, produced noticeable changes in the heating and cooling curves. All of the data reported here were obtained from a sample which had not previously been cycled through the MNM transition and during the run was cycled at an average rate of approximately 0.03 °K/h near the transition.

III. RESULTS AND DISCUSSION

The data were taken from the chart paper at approximately 0.008 °K intervals near the transition and wider intervals away from the transition. It was then punched onto computer cards for analysis. After fitting voltage readings to the thermocouple calibration and making the necessary calculations for the heat input or output, a curve of the enthalpy of the sample versus temperature was constructed and is shown in Fig. 1. It can be seen from this curve that during a cooling run the sample supercools approximately 2.5 °K and that there is considerable hysteresis associated with the transition. The amount of supercooling and hysteresis is increased with much faster cooling rates but is not measurably decreased with slower rates. If fast heating rates are used, a small but measurable amount of superheating is also observed. Because of the supercooling during the cooling run, the transition temperature cannot be determined exactly. We have taken the maximum temperature reached by the sample after supercooling to be the transition temperature for the cooling run, and it is 268.97 °K. In addition, this temperature is within 1.7 °K of the transition temperature obtained from the ratio of the enthalpy to the entropy change across the transition.

The specific heat at constant pressure, C_P, was calculated from the slope of the enthalpy curve, and, for sample No. 2, these data are shown in Fig. 2. In Fig. 3 (see also Fig. 4) the values of C_P near the transition for sample No. 1 with the lattice contribution subtracted for both heating and cooling runs are shown. The data shown for the cooling run are only a portion of the positive parts of the specific heat. Supercooling and subsequent self-heating of the sample occur, giving negative values in addition to double-valued positive specific heats. It can be seen that the cooling curve exhibits sharp discontinuities in C_P due to supercooling. On the heating run such is not the case
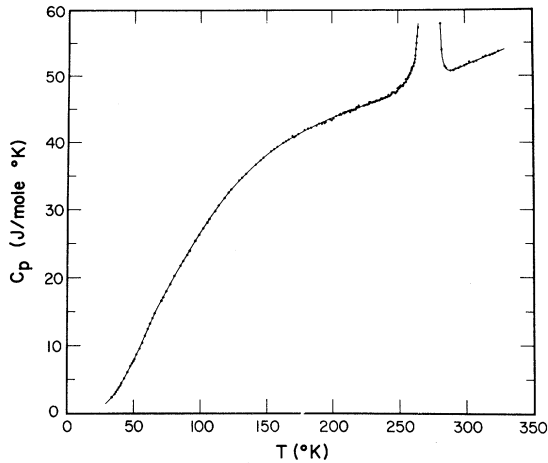
FIG. 2. Heat capacity of sintered NiS pellet as a function of temperature, sample No. 2.

and there are no infinities associated with the heating curve. Broadening of the peak is probably due to inhomogeneity in the sample. A subsidiary peak occurs approximately 0.3 °K below the main peak on the heating curve. An attempt to fit the data to a scaling law applicable to second-order transitions was made. Figure 5 shows the results of this fit for the data both above and below T_c. The function which was fit for this data was $C_P \propto (1 - T/T_c)^{-\alpha}$. It can be seen that the fit for the data on the high-temperature side of the peak is quite good over a large range. The additional peak observed on the low side of the peak causes the data to deviate from a straight line; however, it fits on the same line as the high-temperature data
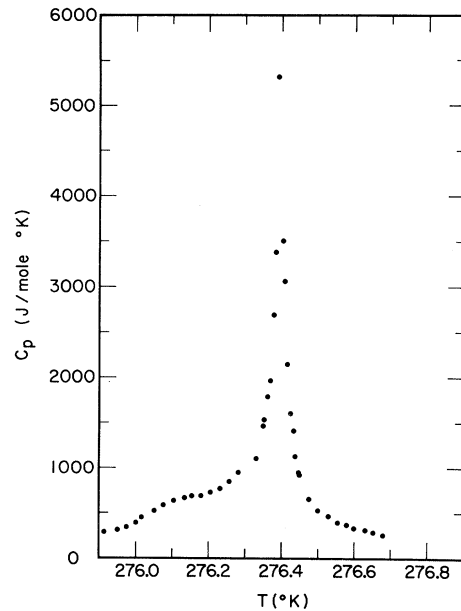

FIG. 4. Detail of the high-temperature peak shown in Fig. 3.

on either side of the subsidiary peak. The value of α obtained from the fit is 0.81 on the high side of the transition.

Both the enthalpy (ΔH) and the entropy (ΔS) changes were computed from the data. For sample No. 1, the lattice contribution to the specific heat was subtracted from the peak by extrapolating the data to the transition temperature from both sides of the peak. The data in the temperature ranges immediately above and below the specific-heat
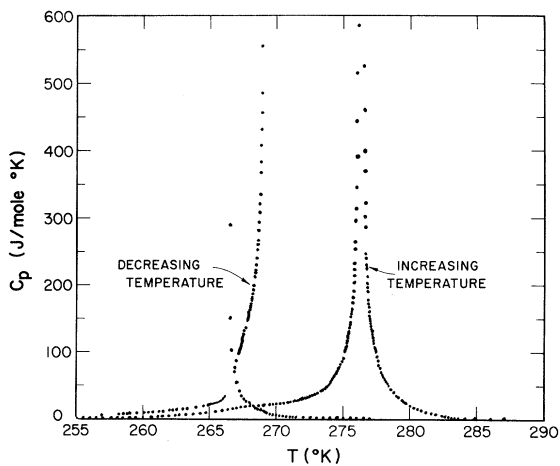

FIG. 3. Heat capacity near the MNM transition in hexagonal NiS, sample No. 1. The transition temperature for the cooling curve has been chosen as the maximum temperature reached after supercooling.
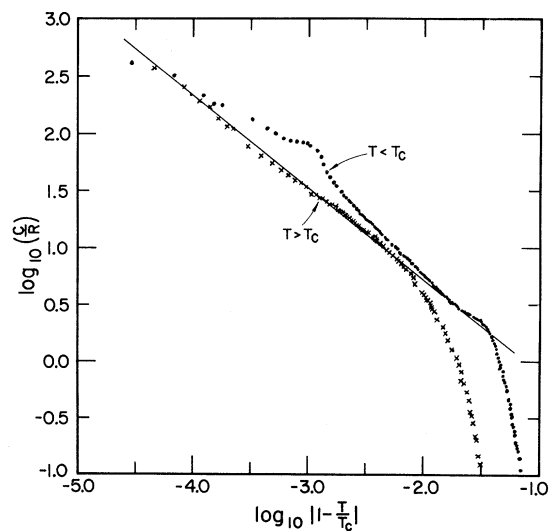

FIG. 5. Dependence of logarithm of the specific heat upon the logarithm of $1 - T/T_c$ for NiS, sample No. 1.

anomaly are linear in temperature within experimental error. From 219 to 253 °K, $C_P(T) = 27.481 + 0.078\,462T$ with a standard deviation of $\sigma = 0.13$. From 278 to 330 °K, $C_P(T) = 31.0165 + 0.067\,876T$ with $\sigma = 0.07$. The data from 278 to 330 °K were taken before lowering the temperature through the transition and were combined with data taken from 288 to 300 °K taken after having cycled the sample through the transition. For the increasing temperature curve, the enthalpy change was found to be 1383 J/mole or 0.0143 eV per Ni atom and the entropy change 5.03 J/mole. This entropy change corresponds to $\Delta S = 0.88R \ln 2$.

There is a possible change in the Debye temperature at the transition because the specific heat increases by 0.61 J/mole deg when the specific-heat data are extrapolated to the transition temperature from both sides of the anomaly. No conclusive statement can be made, however, since the Debye temperature is very sensitive to small errors in C_P in this temperature range and the extrapolation is somewhat arbitrary due to lack of data below 220 °K or above 330 °K for this sample. Also, the only available data for the compressibility and the thermal expansion coefficients are measurements at 77 and 300 °K due to Smith and Sparks[10] and Sparks and Komoto.[4]

IV. CONCLUSIONS

The conclusions that have been drawn from the present measurements are the following:

(a) The MNM transition in NiS displays the characteristics of a first-order transition. The present measurements show the transition to be broadened by inhomogeneities and show considerable hysteresis. The measured enthalpy change (latent heat) at the transition is 1383 J/mole or 0.0143 eV per Ni atom. This result is in agreement with the latent heat computed from the Clapeyron equation which yields 1400 J/mole based on the data of Smith and Sparks[10] and Anzai and Ozawa[11] with a transition temperature of 276.4 °K.

(b) The equilibrium times encountered near the transition are extremely long, and any measurements of the properties of NiS near the transition will require hours at constant temperature to assure equilibrium. An isothermal (± 0.005 °K) measurement of the resistance of the sample on which the C_P measurements were made showed a continuous resistance change for a period of 100 h near the transition temperature. A plot of the resistance ρ vs time in this case fits a functional form of

$$\frac{\rho_\infty - \rho}{\rho_0} = 2.3e^{-(t-t_0)/\tau},$$

with $\tau = 49$ h. Here ρ_∞ is the final-state resistivity and ρ_0 is the resistivity at time $t = t_0$.

(c) The measured entropy change at the transition of $\Delta S = 0.88R \ln 2$ is in good agreement with the conclusions of Sparks and Komoto[7] who measured the sublattice magnetization to be within 90% of its saturation value 4° below the transition. These two results suggest that one electron per Ni atom is involved in the ordering process and that the entropy change is due entirely to the electrons. It should be emphasized that this conclusion is based on the assumption that at the transition the spins merely disorder. If, on the other hand, the localized spins become part of the conduction band at the transition, the value of $\Delta S = 0.88R \ln 2$ must be reinterpreted.

(d) There is a possible change in the Debye temperature at the critical temperature, but no conclusive statement can be made because of the sensitivity of the derived value of the Debye temperature to experimental errors both in measuring C_P and converting to C_V in this temperature range.

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