Pressure-Temperature Phase Diagram and Crystal Structure of NiS

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(Received 8 September 1971)

The antiferromagnetic phase of NiS is suppressed at pressures in excess of 20 kbar and no anomalous behavior is observed in the temperature dependence of the resistivity above the critical pressure. Single-crystal x-ray diffraction studies set a limit on the movement of the sulfur atoms in the antiferromagnetic phase from the centrosymmetric position ($z = \frac{1}{4}$) of $z = 0.252 \pm 0.002$.

NiO is a localized magnetic insulator both above and below its Néel temperature. In contrast, NiS is metallic above its Néel temperature, and the nature of the antiferromagnetic (AF) phase is not yet clear. There is an increase of a factor of 50 in the electrical resistivity at T_N and the temperature coefficient of resistivity is negative just below T_N.[1] At the transition there is a discontinuous increase in both the lattice parameters of the hexagonal NiAs structure,[2] and it has been suggested that there is an accompanying loss of the center of symmetry.[3] This would mean that the Ni and S sublattices are displaced with respect to each other. White and Mott have suggested that the transition in NiS is from semimetal, which is antiferromagnetic, to a "normal" metal.[4] In this model the transition corresponds to a first-order disappearance of the moments on the Ni atoms and not to a disordering of the moments as at a Néel temperature. As the transition temperature decreases rapidly with increasing pressure,[5] we have been able to suppress the AF phase and measure the electrical resistivity of the metallic phase down to liquid-helium temperatures. The absence of any anomalies in the resistivity is interpreted as evidence for the absence of magnetic ordering and therefore of local moments in the metallic phase. Single-crystal x-ray diffraction studies of the AF phase show that the movement of the atoms away from the centrosymmetric positions is near zero, in contrast to earlier reports.[3]

Single crystals of the high-temperature NiAs form were prepared. Equimolar amounts of the elements were sealed in an evacuated quartz tube, using S which had been premelted in vacuum. The tube was then heated over a period of hours to 1000 °C, where the tube was shaken to ensure uniform mixing. After holding for several hours the temperature was lowered at 2 °C/h to 750 °C and then quenched in water to room temperature. From a Guinier x-ray diffraction photograph the product was found to be single phase with lattice parameters $a = (3.4398 \pm 0.0003)$ Å and $c = (5.3482 \pm 0.0005)$ Å. The single-crystal sample was oriented from Laue photographs and bars were cut to measure the re-

sistivity in the [100] direction. Gravimetric analysis indicated a ratio $Ni_{1.01}S_{1.00}$. Cation impurities were < 5 ppm by emission spectroscopic analysis. Sparks and Komoto report that the transition temperature is strongly dependent on the stoichiometry.[1] Our samples order at lower temperatures (235–200 °K) than those reported by some authors (~260 °K).[1,3] From our studies on the preparation of NiS crystals, it is apparent that other variables such as oxygen impurities and quenching temperature must also be considered. A more detailed study is in progress to try to separate these different effects.

The resistivity was measured as a function of temperature at various pressures using a girdle die and cryostat, as described previously.[6,7] The pressure-transmitting medium was AgCl and the pressure calibration was relative to the Bi I-II transition at 25.4 kbar. The results of the experiment on a sample which orders at 230 °K at 1 atm is shown in Fig. 1. The sequence in which the isobars were measured is 28.0, 13.3, 18.7, 19.7, and 2.5 kbar. After the 18.7-kbar isobar the sample was cooled to 4.2 °K at a pressure of 21.8 kbar. When no transition was observed at 21.8 kbar the sample was pressure cycled at 4.2 °K through the transition as shown in Fig. 2 before going on to record the 19.7-kbar isobar of Fig. 1. The 4.2 °K points from each isobar are also shown in Fig. 2. The transition temperature is clearly reversible on pressure cycling.

In a second experiment on a sample which orders at 210 °K the resistivity vs temperature was measured above the critical pressure. Then the sample was repeatedly pressure cycled through the transition, while cooling to and warming from 4.2 °K, in order to determine the pressure-temperature phase boundary. The results are shown in Fig. 3 along with the points from the first experiment. The antiferromagnetic phase is suppressed near 20 kbar. Although the transition temperatures at 1 atm are different for each sample, their critical pressures appear to be the same within experimental error. The initial slope measured by Anzai and Ozawa is shown as the upper
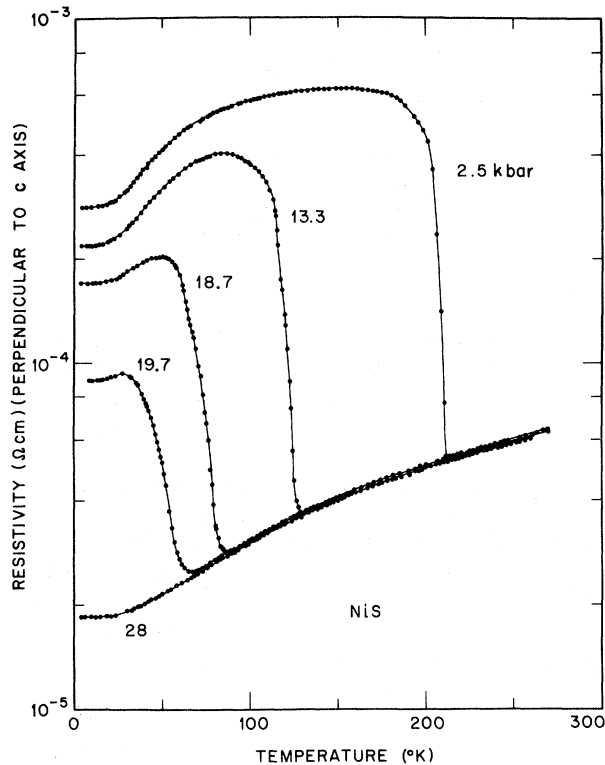
FIG. 1. Resistivity vs temperature at several pressures for a NiS sample which orders at 230 °K at 1 atm.
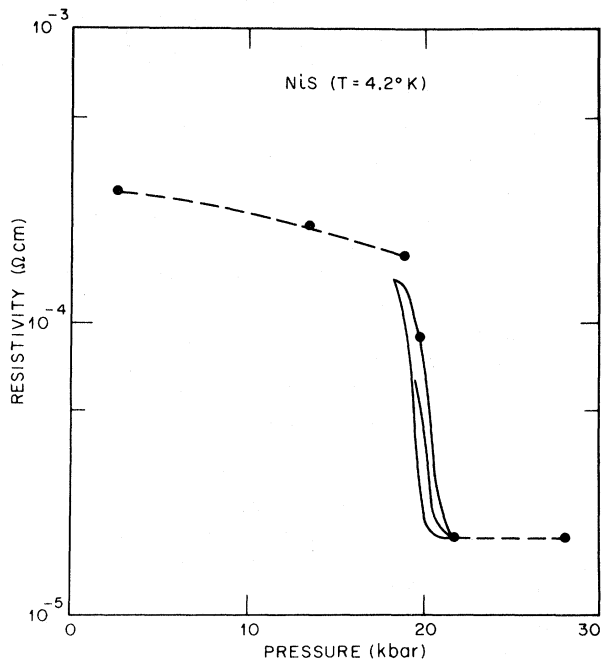

FIG. 2. Resistivity vs pressure at 4.2 °K for sample shown in Fig. 1. Points are terminal points of isobars and continuous curve is from pressure cycling through the transition at 4.2 °K.
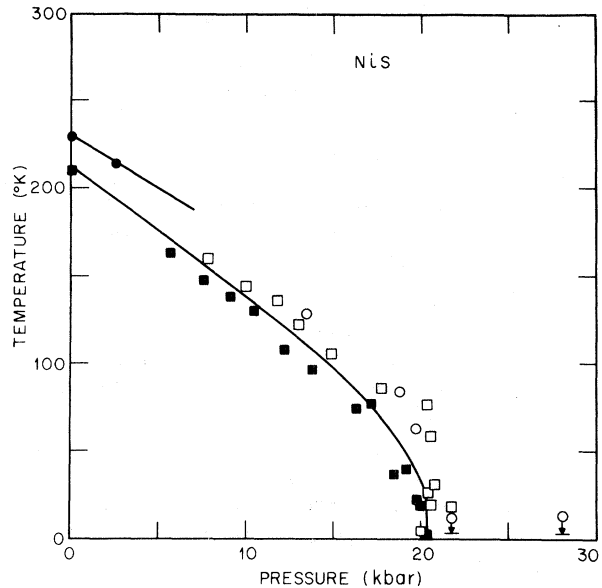

FIG. 3. Pressure-temperature phase diagram for NiS. Open and closed symbols are for increasing and decreasing temperature or pressure. Circles are sample with $T_N = 230$ °K at 1 atm and squares are for sample with $T_N = 210$ °K.

curve in Fig. 3.

The interpretation of the electrical resistivity is complicated by the conversion of part of the sample from the quenched NiAs phase to the stable metallic millerite phase,[8] probably as a result of strains produced during the pressure experiment. An x-ray photograph taken with a Gandolfi camera of the single crystal before the high-pressure runs showed only the lines of the NiAs structure. An upper limit of 2% was estimated for the presence of the millerite phase. In the Gandolfi camera the single-crystal sample is rotated in a random manner to produce a Debye-Scherrer powder pattern. A film of the same single crystal taken after the high-pressure runs contained the strongest lines of the millerite phase together with the pattern corresponding to the NiAs structure. From the intensity of the strongest lines of the two phases it was estimated that after the high-pressure cycling the sample contained at least 5 and possibly as much as 10% of the millerite phase. Similar studies of a sample which had been cycled through the transition at 1 atm showed no millerite phase within detectable limits (< 5%) in the Gandolfi x-ray films. Also, x-ray studies as a function of temperature set a lower limit of > 98% on the fraction of the sample which transformed to the AF phase on cooling. These results suggest that the low resistivity of the AF phase does not result from the presence of a metallic

TABLE I. Comparison between observed and calculated structure factors for the low-temperature structure.

hkl	F_0	centric F_c	acentric F_c
002	22.5	22.8	22.8
004	49.0	50.0	49.9
006	10.2	10.6	10.6
008	27.4	27.1	27.2
0010	6.0	6.0	6.0
0012	16.3	16.3	16.4
0014	5.3	5.0	5.0
110	57.9	57.5	57.6
220	36.0	34.9	35.0
330	22.0	22.4	22.5
440	15.0	15.3	15.5
$R = \sum |\Delta F| / \sum |F_0|$		1.6%	1.6%
scale factor		1.001(8)	0.996(8)
Z_S		0.250	0.252(2)
B_{Ni} (Å^2)		0.20(2)	0.20(2)
B_S (Å^2)		0.15(4)	0.14(4)

second phase in the sample and that NiS in the AF phase is not a good insulator. In the pressure experiment the curves scale at low temperatures as shown in Fig. 1, and it is not clear if this might be due to the presence of some of the millerite phase. However, in the metallic phase this effect is less important. There is no evidence in the resistivity of either sample in the metallic phase for an anomaly as a function of temperature which might reflect magnetic ordering. The temperature dependence of the resistivity is not T^2 at low temperatures as has been found, for example, in V_2O_3,[9] and the metallic phase does appear to be a "normal" metal.

X-ray diffraction studies of NiS were made by cleaving a plate perpendicular to the c axis and by recording the intensities I for the Friedel's pairs of $(00l)$ with $l \leq 14$ and of $(hh0)$ with $h \leq 4$ as a function of temperature. An empirical absorption correction based on the room-temperature data was applied to the low-temperature intensities. No evidence for the breakdown of Friedel's law resulting from the anomalous dispersion effect in noncentrosymmetric crystals was observed in either phase, whereas the positional and thermal parameters reported in Ref. 3 yield measurable ΔF for the weak $(00l)$'s. In the NiAs structure the Ni atoms are at (000) and $(00\frac{1}{2})$ and the S atoms at $\frac{1}{3}\frac{2}{3}z$ and $\frac{2}{3}\frac{1}{3}\frac{1}{2}+z$. If $z = \frac{1}{4}$ then the space group is the centrosymmetric $P6_3/mmc(D_{6h}^4)$ and if $z \neq \frac{1}{4}$,

$P6_3mc(C_{6v}^4)$. In the absence of twinning the measurements above set a limit on the deviation of z from $\frac{1}{4}$ of ± 0.003. However, it is possible that the crystal in the AF phase is multiply twinned, in which case $I(00l) \approx I(00\bar{l})$ for a macroscopic crystal. A least-squares refinement using the average $(00l)$'s and unit weights gave $z = 0.252 \pm 0.002$ and a statistical R factor of 1.6%. A centric refinement based on the same low-temperature data yielded an identical R factor. However, when the observed structure factors for the Friedel pairs $(00l)$ were not averaged, the refinement gave the same positional parameter $z = 0.252 \pm 0.002$ and an R factor of 2.0%. Table I shows the agreement between the observed and calculated structure factors for the two low-temperature models. Within experimental error there is no detectable loss of the center of symmetry at the Néel temperature. These results are in marked contrast to those of Trahan et al., who report a parameter of 0.275 ± 0.007 at 77 °K from a refinement of powder-x-ray diffraction data.[3] By using their data we found that the weighting scheme in the refinement was highly critical in the determination of the positional parameter. For instance, by using unit weights one obtains a positional parameter for sulfur $z = 0.258 \pm 0.013$.

The present experiments at high pressure establish a critical pressure for antiferromagnetism in NiS of ≈ 20 kbar. The resistivity-vs-temperature curve above P_c does not show any anomalies which would be expected if the metallic phase exhibited any magnetic ordering at low temperatures. This suggests the absence of static magnetic moments in the metallic phase, which is compatible with the neutron-diffraction studies [10] and the model of White and Mott.[4] These authors also suggest that the AF phase of NiS is not localized like NiO, and the low resistivity of the AF phase favors this view. The earlier powder-x-ray results led them to suggest that a shift of the Ni planes with respect to the S planes caused the nickel e_g subband to shift with respect to the sulfur p bands. The present results show that this shift is extremely small if it exists at all. They also show that any change in band structure must come from magnetic effects or from the change in c/a lattice-parameters ratio rather than from shifts of the atoms within the unit cell.

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Equilibrium States of the Ising Model in the Two-Phase Region

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(Received 30 August 1971)

We prove that at low enough temperature all translationally invariant equilibrium states for the Ising ferromagnet are a superposition of only two extremal states, i.e., the positively and negatively magnetized pure phases. In particular this proves, at low temperature and in two dimensions, the identity of the spontaneous magnetization and the Onsager's value $M_0 = [1 - (sh\beta)^{-4}]^{1/8}$.

I. INTRODUCTION

Consider an Ising ferromagnet enclosed in a box Λ in a square lattice. Assume that if $\underline{\sigma}$ is a spin configuration, then its energy is given by

$$H_0(\underline{\sigma}) = -\frac{1}{2} \sum_{\langle ij \rangle} \sigma_i \sigma_j , \qquad (1)$$

where $\sum_{\langle ij \rangle}$ denotes, as usual, the sum over the nearest-neighbors pairs in Λ. We have put the strength of the interaction $J = -\frac{1}{2}$ for simplicity, and the external magnetic field $h = 0$, since we are interested in the two-phase region.

Suppose also that fixed spins $\underline{\tau}$ are placed on the lattice sites adjacent to the boundary of Λ and define

$$H_{\underline{\tau}}(\underline{\sigma}) = -\frac{1}{2} \sum_{\langle ij \rangle} \sigma_i \sigma_j - \frac{1}{2} \sum_i \sigma_i \tau_i - \frac{1}{2} \sum_{\langle ij \rangle} \tau_i \tau_j , \qquad (2)$$

where the second sum runs over the couples of spins (σ_i, τ_i) adjacent to the boundary; the last term in (2) is $\underline{\sigma}$ independent and has been added only for convenience.

If $p_\Lambda(\underline{\tau})$ is a probability distribution over the set $\underline{\tau}$, we define the probability of a spin configuration $\underline{\sigma}$ as

$$P(\underline{\sigma}) = \sum_{\underline{\tau}} (e^{-\beta H_{\underline{\tau}}(\underline{\sigma})} / \sum_{\underline{\sigma}'} e^{-\beta H_{\underline{\tau}}(\underline{\sigma}')}) p_\Lambda(\underline{\tau}) . \qquad (3)$$

It will be more convenient to introduce instead of $P(\underline{\sigma})$ the set of correlation functions

$$\langle \sigma_{x_1} \cdots \sigma_{x_n} \rangle_{p_\Lambda} = \sum_{\underline{\sigma}} \sigma_{x_1} \cdots \sigma_{x_n} P(\underline{\sigma}) ,$$

$$n = 1, 2, \ldots ; \quad x_1, x_2, \ldots \text{ in } \Lambda . \qquad (4)$$

We shall be interested in the set of functions $\langle \sigma_{x_1} \cdots \sigma_{x_n} \rangle$ which can be written [for a suitable choice of $p_\Lambda(\underline{\tau})$] as

$$\langle \sigma_{x_1} \cdots \sigma_{x_n} \rangle = \lim_{\Lambda \to \infty} \langle \sigma_{x_1} \cdots \sigma_{x_n} \rangle_{p_\Lambda} , \quad n = 1, 2, \ldots \qquad (5)$$

for all $x_1, \ldots, x_n$ in the lattice, and furthermore are such that

$$\langle \sigma_{x_1 + a} \cdots \sigma_{x_n + a} \rangle \equiv \langle \sigma_{x_1} \cdots \sigma_{x_n} \rangle \text{ for all } a . \qquad (6)$$

A set or correlation functions verifying (5) and (6) will be called an equilibrium state at temperature β^{-1}.

At β large enough it is known that there are at least two different equilibrium states, which will be denoted as $\langle \sigma_{x_1} \cdots \sigma_{x_n} \rangle^+$ and $\langle \sigma_{x_1} \cdots \sigma_{x_n} \rangle^-$. These states can be obtained by choosing in (5) the distribution $p_\Lambda(\underline{\tau})$ to be, respectively,

$$p_\Lambda^{\pm}(\tau) = \prod_i \delta_{\tau_i, \pm 1} , \qquad (7)$$

i.e., by fixing the boundary spins to be all up or all down. These states have very special physical properties,[1] which explain why they are usually called the up-magnetized and the down-magnetized pure phases; for instance,

$$\langle \sigma_{x_1} \cdots \sigma_{x_n} \rangle^+ = (-1)^n \langle \sigma_{x_1} \cdots \sigma_{x_n} \rangle^- ,$$

$$\langle \sigma_{x_1} \cdots \sigma_{x_n} \rangle^+ = \lim_{h \to 0^+} \langle \sigma_{x_1} \cdots \sigma_{x_n} \rangle_h ,$$