Pressure-Induced Metallization and the Collapse of the Magnetic State in the Antiferromagnetic Insulator NiI$_2$

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The first observation of a pressure-induced metallization accompanied by the spontaneous collapse of magnetic ordering is reported. This isostructural concurrence is observed in the layered antiferromagnetic insulator NiI$_2$. Electrical transport, x-ray-diffraction, and ^{129}I Mössbauer studies were carried out in diamond-anvil cells. The evidence points to a mechanism by which the originally *filled* 5p-iodide band shifts and overlaps with the *partially* filled nickel-3d states. The formation of a hybridized conduction band at $P > 19$ GPa results in the onset of a diamagnetic metallic ground state.

Many of the insulating transition-metal and rare-earth compounds have localized magnetic moments that result from strong electron correlations and the partial filling of the 3d and 4f states, respectively. The nature of the magnetic ordering of these substances and the corresponding ordering temperatures are determined by various exchange and superexchange mechanisms.[1-3] The application of hydrostatic pressure results in increased wave-function spatial overlaps, which is the cause of band shifts, overlaps, and broadening, and of stronger band hybridization. All of these effects may lead to delocalization of the electronic wave function and hence metallization, and, in principle, to the disappearance of the magnetic moments.[4,5]

Experimental studies to verify the close relationship between energy-gap closure, magnetic properties, and crystallographic structure changes induced by high pressure are scarce. The reason is primarily the lack of suitable tools for probing magnetism at very high pressures. The only extensive studies reported so far[6,7] are in the ferromagnetic semiconductor EuO. No study, however, has shown evidence for the total collapse of magnetic ordering. This Letter reports the first observation of a pressure-induced destruction of magnetic ordering which occurs concurrently with an *isostructural* insulator-metal transition. This phenomenon occurs in NiI$_2$, a layered antiferromagnetic insulator under ambient pressure with Néel temperature $T_N = 75$ K.

Nickel iodide crystallizes in the CdCl$_2$ ($R\bar{3}m$) structure, a trigonal layered structure which consists of strongly bound triple slabs of I$^-$-Ni^{2+}-I$^-$ which interact weakly with each other. In the hexagonal lattice each unit cell contains three formula units stacked in a staggered fashion along the c axis. The lattice constants are $a = 3.82$ Å and $c = 19.81$ Å. The magnetic structure, as determined by neutron diffraction,[8] is a helix-1 type, with spins ordered ferromagnetically in each Ni^{2+} layer,

and with all spins lying in a plane which makes an angle of about 55° with the c axis. This antiferromagnetic alignment of ferromagnetically ordered a-b planes is consistent with previous Mössbauer data.[9] The magnetic moment of Ni^{2+} in NiI$_2$ is 1.6μ_B. Band-structure calculations of the Ni halides[10] yield a fully occupied 5p-iodine band and a partially filled 3d-nickel band, i.e., a 3d transition metal. The system, however, is a Mott insulator similar to NiO and CoO. This conclusion was reached by Pollini, Thomas, and Leselink[11] who analyzed their nickel halide optical data by means of a ligand-field theory. They interpret the observed reflection peaks at 2-3 eV as arising from the excitonic transitions 5$p^6$3d^8 to 5$p^5$3d^9. Photoconductivity measurements by Ronda, Arends, and Haas[12] yield a conductivity energy gap of 1.9 eV.

Diamond-anvil-cell (DAC) Mössbauer spectroscopy (MS) has been shown to be a unique method for studying pressure-induced phenomena on the atomic scale.[13] The present work is the first application of the *transferred hyperfine interaction*[14] (THI) to high-pressure magnetic studies. The THI observed in I$^-$ is a consequence of the polarization of its valence 5s electrons induced by the Ni^{2+} magnetic moments. Because of the crystal symmetry, the hyperfine field H_{hf} at the ^{129}I nucleus is determined by the three nearest Ni neighbors, all situated in the same ferromagnetically ordered sublayer. Thus the THI allows the layer sublattice magnetization to be studied as a function of pressure and temperature.

Samples of NiI$_2$ were prepared by direct synthesis from the elements. For the MS studies, elemental iodine enriched with 83% of ^{129}I was used. The samples were loaded into the DAC under an inert-gas atmosphere. For the MS studies a modified Merrill-Bassett DAC was used in conjunction with a TaW alloy as a gasket and collimator and with Ar as the pressure medium.[13] For

the resistance and angle-dispersive x-ray measurements, a Mao-Bell-type DAC was used. The resistance was measured using a quasi-four-point method[15] with $CaSO_4$ as the pressure medium. The x-ray diffraction was carried out with monochromatic Mo $K\alpha$ radiation and with no pressure medium. Measurements were carried out in the pressure and temperature ranges of 0-35 GPa and 4-300 K, respectively, with the exception of the x-ray experiments, for which data were recorded at room temperature. Pressures were measured with the ruby-fluorescence method.[16] Uncertainties in pressures did not exceed 1 GPa.

The experimental MS spectra were interpreted with the following spin Hamiltonian:

$$H = \mu H_{hf}(I_z/I) + \{ \tfrac{1}{2} e^2 q_{zz}Q(3\cos^2\Theta - 1)/4I(2I-1)\}$$
$$\times \{3I_z^2 - I(I+1)\}, \qquad (1)$$

where H_{hf} is the hyperfine field, $e^2 q_{zz}Q$ is the quadrupole coupling, and Θ is the angle between the principal axis of the electric-field gradient (eq_{zz}) and H_{hf}. With $\Theta = 55° \pm 10°$, the contribution of the quadrupole interaction at temperatures below T_N vanishes, and the absorption

spectrum becomes symmetric. Typical spectra for $P = 6.7$ GPa at various temperatures are shown in Fig. 1, curves a-d. Figure 1, curve a, corresponds to a saturation field $H_{hf} = 265$ kOe and curve d to the paramagnetic state. Figure 1, curve e, corresponds to $P = 26.3$ GPa. There the system exhibits no magnetic interaction. At each pressure T_N was determined by extrapolation.

The variation of T_N, the saturation field (H_{hf}), and the isomer shift (IS) of NiI_2 with volume are shown in Fig. 2. The H_{hf}, which is a measure of the unpaired-spin density at the ^{129}I 5s orbitals, remains constant up to $P = 13$ GPa $(\Delta V/V_0 = 0.24)$. In the pressure range of 13-19 GPa it decreases by 17% gradually and at $P_c = 19$ GPa $[(\Delta V/V_0)_c = 0.27]$, H_{hf} suddenly drops to zero. The disappearance of the magnetic interaction at $P > P_c$ indicates the collapse of the antiferromagnetic ground state. As can be seen, T_N increases by a factor of 4 from 75 K at $P = 0$ to 310 K at $P = 19$ GPa and is linear with $\Delta V/V_0$. The IS, a measure of the iodine 5s density at the nucleus, increases linearly with decreasing volume, and shows no discontinuity at P_c. No hysteresis has been detected.

The x-ray-diffraction measurements provide unit-cell dimensions $a(P)$ and $c(P)$, and consequently the unit-cell volume $V(P)$. Figure 3 shows a plot of specific

FIG. 1. The ^{129}I Mössbauer spectrum of NiI_2. The source is $Mg_3^{129m}TeO_6$. Curves a-d correspond to spectra recorded at 6.7 GPa at various temperatures. The spectrum shown in curve e was recorded at 26.3 GPa at $T = 44$ K and corresponds to the *diamagnetic* state of NiI_2. The solid line is a theoretical spectrum obtained from the least-squares fit of the spin Hamiltonian.
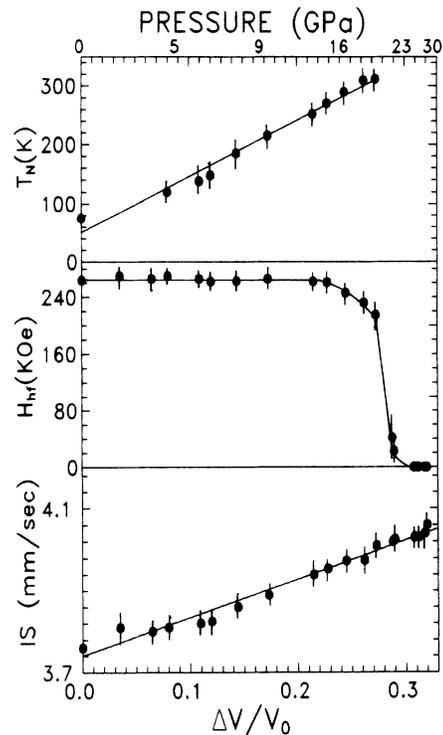
FIG. 2. The Néel temperature T_N, the saturation hyperfine field $H_{hf}(T=0)$, and isomer shift (IS) $(T=300$ K) as a function of $\Delta V/V_0$, where $\Delta V = V(0) - V(P)$. Values for $\Delta V/V_0$ were derived from the experimental equation of state. The linear curves are least-squares fits. The solid curve in the middle graph is for eye-guiding purposes only.
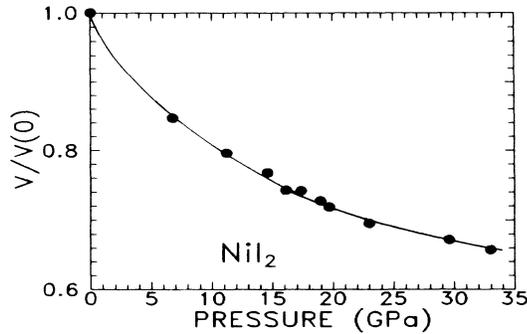
FIG. 3. The normalized volumes vs pressure at $T = 300$ K as measured by angle-dispersive x-ray diffraction. The solid curve is a least-squares fit with the Birch-Murnaghan equation of state which yields values for the bulk modulus and its pressure derivatives of $K_0 = 27.7(0.9)$ GPa and $K_0' = 4.8(0.2)$, respectively. The uncertainties (Ref. 23) in $V/V_0(P)$ are ± 0.003.

FIG. 4. The variation of $\log_{10}R$ with volume at $T = 300$ K. The curve is linear up to $\Delta V/V_0 \approx 0.25$, above which it drops rapidly, reaching a plateau near P_c. Inset: Temperature dependence of the resistance normalized at 77 K. Curve a corresponds to the semiconductor antiferromagnetic state at $P = 17.5$ GPa and curve b to the metallic diamagnetic state at $P = 21$ GPa.

volume, normalized to $V(0)$, versus pressure. No transition to another crystallographic state at P_c is observed and $V/V(0)$ varies smoothly with pressure, with no discontinuity. This indicated unequivocally that, within the experimental error and up to 35 GPa, NiI_2 exhibits no first-order phase transition.

The volume dependence of the resistance R in logarithmic scale is shown in Fig. 4. For $P < 17$ GPa, $\log_{10}R$ decreases linearly with $\Delta V/V_0$, and near P_c it drops rapidly and levels off at $P > P_c$. The leveling of $\log_{10}R$ at P_c suggests a transition from an insulator to a metal. This is confirmed by comparing the temperature dependence of R below and above P_c. The inset shows the temperature dependence of R at 17.5 GPa $(P < P_c)$ and at 21 GPa $(P > P_c)$, which clearly demonstrates the transition from a gap to gapless electronic behavior.

The interactions responsible for the antiferromagnetic structure and for the value of T_N are the various quantum-mechanical exchanges: direct, indirect, and superexchange. The linear dependence between T_N and $\Delta V/V_0$ simply reflects the increase with decreasing volume of the wave-function overlap which affects the various exchanges. The fact that no special features are observed in the $T_N(V)$, $IS(V)$, and $\log_{10}R(V)$ curves suggests that the characteristics of the ambient-pressure wave functions, and therefore the qualitative properties of the energy bands, are preserved under pressure.

Photoemission experiments[17,18] in NiF_2 and the layered Ni halides[12] and optical studies[18] in antiferromagnetic (rocksalt structure) NiO indicate that the most energetic electrons in these Mott-insulating-type materials are the correlated nickel $3d$ states with the anion p states lying 1 eV or less below them. The carrier activation energy for the pure specimens in either a $3d^8$ to $3d^7 4s^1$ transition[19,20] as in NiO, or a $5p^6 3d^8$ to $5p^5 3d^9$ transition as in the layered Ni-halide compounds. For NiI_2 the conductivity gap[18] was found to be 1.9 eV.

Reflectivity measurements[21] in NiI_2 were interpreted

as resulting from the excitonic $5p^6 3d^8$ to $5p^5 3d^9$ narrow transition at approximately 2 eV followed by a broad $5p^6 3d^8$ to $5p^5 3d^9$ band at 2.5-4 eV, and a $5p^6 4s^0$ to $5p^5 4s^1$ transition at 6-7 eV. The "conductivity" gap can be interpreted to be the $5p^6 3d^8$ to $5p^5 3d^9$ broad transition, in which the p hole is extended and the d electron essentially localized. If it were not for the strong Coulomb repulsion among the $3d$ electrons, which through correlations produce a Mott insulator, the electronic properties of NiI_2 would result in a metallic state. Although no band-structure calculations exist for NiI_2, the known ones for the isostructural $NiCl_2$ and $NiBr_2$ yield the following characteristic features: (i) a fully occupied halogen p band whose topmost energy is at the Brillouin zone center and whose widths are 3 and 5 eV in $NiCl_2$ and $NiBr_2$, respectively; (ii) a manifold of five Ni $3d$ bands in the energy ranges of 0.35-1.9 and 0-1.5 eV for the chloride and bromide, respectively; (iii) a very wide set of unoccupied bands, arising predominantly from the Ni $4s$ band, starting at 5.9 and 3 eV in $NiCl_2$ and $NiBr_2$, respectively.

Following the above trends it is reasonable to expect that the Ni $3d$ bands would have even lower energy in NiI_2. As P increases the overlap between bands increases, and while the Mott insulator remains the lowest-energy state, the iodine-mediated interaction, i.e., the superexchange responsible for the antiferromagnetism, increases and thus produces the observed fourfold increase in T_N. The superexchange is proportional[22] to the electron "hopping" energy between the Ni^{2+} and I^- to the fourth power, which also increases with pressure.

At $P = P_c$ the energies of the "localized-d-orbital" Mott insulator and the "extended-d-orbital" correlated metal become equal, with the latter becoming the ground state for $P > P_c$. In this metallic regime the band-structure picture[10] becomes valid, and the combined, highly hybridized 11 pd bands (22 spin bands) occupied by 20 electrons should result in an even-valence diamagnetic metal with no magnetic moment at the Ni sites. The conclusion is that the observed phenomena can be considered as a pure insulator-metal transition, accompanied by an antiferromagnetic-diamagnetic transition.

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