# Closure of the Charge-Transfer Energy Gap and Metallization of $NiI_2$ under Pressure

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We have performed resistivity and near-ir absorption measurements on $NiI_2$ under pressure that strongly suggests that closure of the charge-transfer energy gap is the fundamental cause of the insulator-to-metal transition in $NiI_2$. Our findings support the framework proposed by Zaanen, Sawatsky, and Allen outlining the electronic structure of transition-metal compounds.

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Recently a pressure-induced insulator-metal (IM) and antiferromagnetic-nonmagnetic phase transition has been reported in the antiferromagnetic insulators $NiI_2$ [1] and $CoI_2$ [2]. This transition is interesting because it is purely electronic and electronic phase transitions are important for understanding the properties of highly correlated electron systems. It was believed that many transition-metal compounds are insulators (known as Mott-Hubbard insulators) because of their large on-side *d-d* Coulomb repulsion, $U$ [3,4]. In 1984 Zaanen, Sawatzky, and Allen (ZSA) pointed out that a large $U$ is only a necessary condition for a finite transport gap. ZSA proposed a more general model [5] in which the minimum transport gap can also be determined by the charge-transfer energy ($\Delta$), the energy necessary to excite an electron from the anion valence band to the transition metal ion. Zaanen, Westra, and Sawatzky concluded that the nickel dihalides are examples of such charge-transfer insulators [6].

There is still uncertainty in the mechanism responsible for the IM transition in $NiI_2$. Metallization can occur by delocalization of the $d$ electrons [4] as $U \rightarrow 0$. The temperature driven IM transitions in $V_2O_3$, $VO_2$, and $Ti_2O_3$ are prime examples [3,4,7]. In the second scenario, closure of the charge-transfer gap (CTG) resulted in metallic conductivity via creation of ligand holes. Recently metallization by closure of CTG induced by temperature has been reported in $RNiO_2$ (where $R$=rare earth) perovskites [8]. On the other hand, theoretical studies of $NiI_2$ have essentially assumed that the IM transition is driven by CTG closure [9,10]. However, Mössbauer spectroscopy shows no discontinuous charge transfer between Ni and I ions [1]. Since these two IM transition mechanisms have the same signatures but are fundamentally different, a method for differentiating them is desirable.

In this paper we report resistivity and absorption measurements of $NiI_2$ up to 22 GPa. Our results strongly suggest that closure of the CTG is the cause of the pressure-induced IM transitions in $NiI_2$.

$NiI_2$ is an antiferromagnetic insulator at ambient pressures with a Néel temperature of 75 K. It crystallizes in the $CdCl_2$ ($R\bar{3}m$) structure. Small platelets of the crystal were grown from the elements by vapor transport method inside a quartz ampoule and cleaved perpendicular to the crystal's $c$ axis into thin sheets approximately 10 $\mu$m thick. These thin sheets were loaded into a diamond-anvil high pressure cell for absorption measurements without further treatment. The pressure medium was nitrogen in the absorption measurements and a soft powder ($CaSO_4$) in the electrical measurements. Ruby fluorescence was used to determine the pressure. The pressure inhomogeneity was estimated to be better than $\pm 3\%$ in the optical measurements and about $\pm 8\%$ in the electrical experiment.

Near-ir measurements (0.8 to 2.5 $\mu$m) were performed at room temperature using a $\frac{1}{4}$ m grating monochromator and a quartz halogen lamp. Light from the lamp was modulated by a chopper before being focused into the spectrometer. Mirror optics were used to minimize chromatic aberration. Light transmitted by the sample was detected by a PbS photoconductor and a lock-in amplifier. The spectral resolution was estimated to be 20 meV. No correction was made for reflectivity of the sample since it should not be significant in regions where the sample was strongly absorbing. The overall signal-to-noise ratio was sufficient to measure absorbance (absorption coefficient times sample thickness) between 0.1 and 6.

We have extended the measurement of the resistivity in $NiI_2$ over a larger range of temperatures and pressures than in Ref. [1]. Instead of the quasi-four-probe method [11], resistance in the plane perpendicular to the $c$ axis was measured with a four-probe technique [12,13]. The resistivity was estimated from the measured resistance and approximate sample sizes (typically about $50\times 50 \times 10$ $\mu m^3$). Measurements were performed under two different conditions: Either the sample pressure was increased at room temperature or the sample pressure was set at room temperature and then the cell was cooled to

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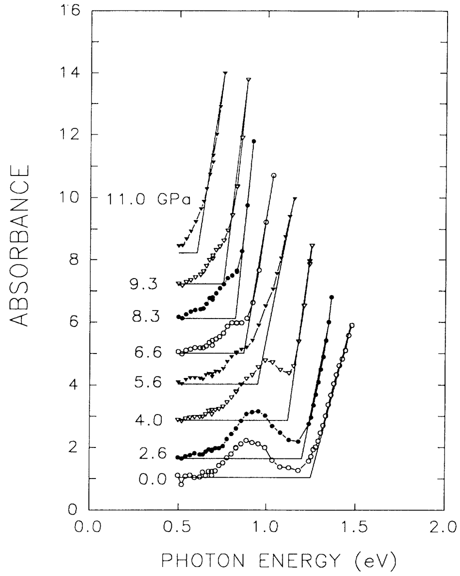

FIG. 1. Absorbance spectrum of $NiI_2$ as a function of pressure. The resolution is 20 meV. The straight lines show how we determined the absorption edge. The spectra are displaced vertically relative to each other by one unit to facilitate viewing. The sample thickness was about 10 $\mu$m, so one unit of absorbance corresponds roughly to an absorption coefficient of $10^3$ $cm^{-1}$.

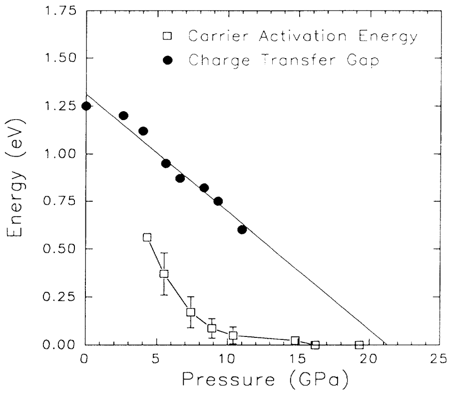

FIG. 2. Charge-transfer gap $E_{\mathrm{CTG}}$ and carrier activation energies as a function of pressure. The line through $E_{\mathrm{CTG}}$ data is a least-squares fit. Lines through the carrier activation energy data are guides for the eye.

liquid helium temperatures. Each experiment typically involves a different sample because usually samples cannot be recovered after compression. As a result resistivity values determined in different runs cannot be compared on an absolute scale due to uncertainties in sample sizes and shapes. In addition, thermal contraction of the cell increased the pressure by about 10% on cooling from room temperature to 4 K.

Figure 1 shows the absorbance spectra of $NiI_2$ at various pressures for light polarized perpendicular to the $c$ axis. The spectra have been displaced vertically for clarity. The atmospheric pressure spectrum contains two important features: a steeply rising absorption edge at 1.2 eV and a small broad peak at approximately 0.9 eV. Previous studies of Ni dihalides [14–17] have ascribed the absorption edge to the charge-transfer transition from the valence band, composed essentially of iodine $5p$ orbitals, to the nickel $3d^8$ bands (written symbolically as $3d^8$-$3d^8 \rightarrow 3d^8\underline{L}$-$3d^9$ where $\underline{L}$ represents a ligand hole [5]). The lower energy peak has been attributed to phonon-assisted ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transitions within the crystal-field split $Ni^{2+}$ $3d^8$ states [14–16]. These identifications are consistent with the large oscillator strength of the electric-dipole-allowed charge-transfer transition and the weaker electric-dipole-forbidden transitions within the $3d^8$ multiplets. They also agree with the trend in the absorption spectra of Ni dihalides when the halogen is varied from Cl to I [14,15]. While the $Ni^{2+}$ $3d^8$ transitions are unaffected by changing the halogen atoms, the CTG increases from 4 eV in $NiCl_2$ to 1.2 eV in $NiI_2$ because of decrease in the anion electron affinity.

On increasing pressure the charge-transfer absorption edge shifts to lower photon energies. To determine the energy of the charge-transfer gap ($E_{\mathrm{CTG}}$) we have simply extrapolated the absorption edge to the background absorption level as shown schematically in Fig. 1. This procedure is adequate in determining the pressure dependence of $E_{\mathrm{CTG}}$ since the absorption edge shifts uniformly with pressure. The resultant pressure dependence of $E_{\mathrm{CTG}}$ is shown (closed circles) in Fig. 2. By fitting the data points to a straight line we find that $E_{\mathrm{CTG}}$ *decreases* with pressure at the rate of −62 meV/GPa and extrapolates to zero at 21 GPa.

In the ZSA framework $E_{\mathrm{CTG}}$ is related to the charge-transfer energy, $\Delta$, and the bandwidth, $W$, of the anion $5p$ valence band by the equation

$$E_{\mathrm{CTG}} = \Delta - W/2 + 2\delta_0 - \delta_{-1} - \delta_{+1}\,, \qquad (1)$$

where $\delta_0$, $\delta_{-1}$, and $\delta_{+1}$ are hybridization shifts of the $3d^8$, $3d^8\underline{L}$, and $3d^9$ electron configurations, respectively [18]. We can estimate the pressure dependence of $E_{\mathrm{CTG}}$ from Eq. (1). $\Delta$ is essentially the electron affinity of the anion minus the ionization energy of the cation plus an electrostatic Madelung term. Its pressure dependence is estimated to be smaller than that of the other terms in Eq. (1) [19]. The pressure dependence of the I $5p$ bandwidth $W$ can be estimated within the tight-binding approximation. If we assume that $W$ is ~5 eV at atmospheric pressure from photoemission measurements and band structure calculations [20,21], and $W$ varies as $V^{-2/3}$, then using the $P$-$V$ data in Ref. [1] we arrive at $d(-W/2)/dP = -37$ meV/GPa which is only 60% of the value $dE_{\mathrm{CTG}}/dP = -62$ meV/GPa. The difference may be attributed to the pressure dependence of the hybridization shifts which are difficult to estimate [22].

Nevertheless we can conclude that a significant contribution to the decrease in the energy required to excite electrons from the $3d^8$-$3d^8$ to the $3d^8\underline{L}$-$3d^9$ configuration with pressure comes from the broadening of the iodine $5p$ bands. Although we were not able to measure values of $E_{\rm CTG}$ less than 0.5 eV, the lack of any evidence of a structural transformation strongly suggests that $E_{\rm CTG}$ will continue to decrease with pressure.

The resistivity measurements provide additional information on the IM transition. Figure 3 shows the room temperature resistivity of $\mathrm{NiI_2}$ as a function of pressure. For $P < 15$ GPa the resistivity decreases exponentially. Around 16.5 GPa a distinct knee appears and is reproducible over several runs using different $\mathrm{NiI_2}$ samples. Above 18 GPa the resistivity becomes almost independent of pressure. Figure 4 shows the Arrhenius plot of the resistivity results. For $P < 16.2$ GPa the resistivity exhibits activated behavior. The slopes of the Arrhenius plots in this pressure range are not constant but rather suggest a range of activation energies. The activation energies are deduced from the resistivity curves in Fig. 4 by the equation

$$\rho = \rho_0 \exp(E_t/2kT)\,, \tag{2}$$

where $\rho_0$ is the high temperature resistivity, $E_t$ is the transport activation energy, $k$ is Boltzmann's constant, and $T$ is the temperature. The values of $E_t$ determined in this way are shown as open squares in Fig 2. The vertical bars in Fig. 2 indicate the range of activation energies deduced from the Arrhenius plots. At $P=5$ GPa, $E_t$ is on the order of 0.5 eV, which is significantly smaller than $E_{\rm CTG}$ at the same pressure. $E_t$ decreases with pressure at an initial rate of $\sim -110$ meV/GPa, decreases more slowly above 10 GPa, and then extrapolates to zero around 16 GPa. Although $E_t$ does not follow $E_{\rm CTG}$, it remains always less than $E_{\rm CTG}$ and both decrease monotonically. It is thus plausible that $E_t$ is determined by defects levels within the CTG. We observe these levels only in resistivity because of the low sample temperature. $E_t$ cannot be a measurement of $U$ since the value of $U$ determined from photoemission at ($\sim$6 eV) is much larger than the value of $E_t$ extrapolated to atmospheric pressure from Fig. 2. In the inset of Fig. 3 we show the resistivity of $\mathrm{NiI_2}$ versus temperature on a linear scale at 16.2 and 19.3 GPa. In both curves the resistivity increases almost linearly with temperature as expected for a metal except for the small dip at very low temperature in the 16.2 GPa curve. Measurements performed at high pressures all showed metallic behavior similar to the 19.3 GPa run.

The resistivity vs pressure data (Fig. 3) can also be interpreted using Eq. (2). If $\rho_0$ is assumed to be independent of pressure and $E_t = \alpha(P-P_0)$ for $P<P_0$ (the gap closure pressure), the resistivity would decrease exponentially with pressure for $P<P_0$. Once $E_t \rightarrow 0$ further increase in carrier concentration would be weaker and hence the resistivity would be relatively independent of pressure. Thus the data in Fig. 3 suggest that $P_0 \approx 18$ GPa. We also note that $\alpha = dE_t/dP$ as determined from the slope of the data points for $P<12$ GPa is $\sim -50$ meV/GPa in good agreement with $dE_{\rm CTG}/dP$ determined from the absorption data. In addition, the estimated conductivity at 18 GPa ($2\times10^3$ $\Omega^{-1}\mathrm{cm}^{-1}$) is near the minimum value of metallic conductivity ($\sim 10^3$ $\Omega^{-1}\mathrm{cm}^{-1}$) [4].

Temperature dependent resistivity (inset of Fig. 3) places the metallization pressure between 16 and 18 GPa. However, the extrapolated $E_{\rm CTG}$ from absorption measurements closes at 21 GPa. The differences between the resistivity and the absorption measurements can partly be

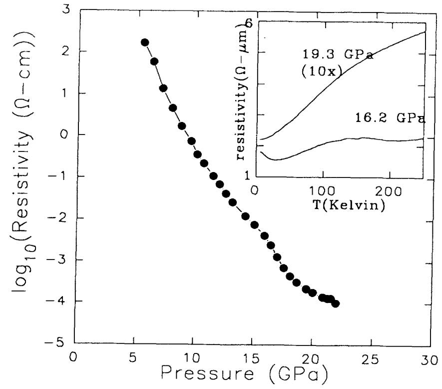

FIG. 3. Room temperature resistivity of $\mathrm{NiI_2}$ versus pressure. The lines are drawn as guides for the eye. Inset shows resistivity vs temperature on a linear scale at $P=16.2$ and 19.3 GPa. The "10×" indicates that the data at 19.3 GPa in the inset were multiplied by 10 so that they can be plotted on the same scale as the 16.2 GPa data. Because of the uncertainty in sample dimensions, resistivity deduced from different samples may be different.

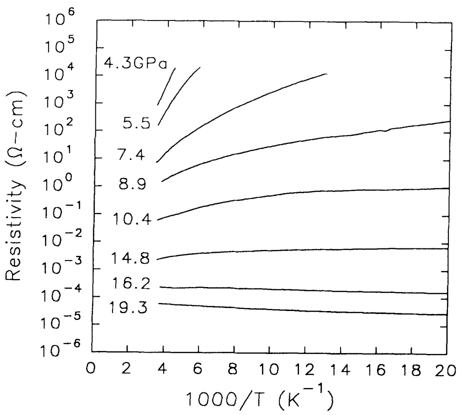

FIG. 4. Temperature dependent resistivity of $\mathrm{NiI_2}$ plotted in Arrhenius format. Note activated behavior at 14.8 GPa and metallic conductivity at 19.3 GPa. The 16.2 GPa run exhibits mixed behavior and is very close to the metallization pressure.

attributed to the different pressure mediums used. In resistivity measurements, the inherent quasihydrostaticity of the medium can change the transition pressure [13]. Nevertheless, both $E_{\rm CTG}$ and resistivity show the same trend towards a metallic behavior at high pressure. Although resistivity measurements are influenced by defects, the closure of $E_{\rm CTG}$ will imply the closure of any gap between defect states and band states. These considerations strongly suggest that *the metallization in NiI$_2$ is fundamentally driven by the closure of the charge transfer energy gap.* Closing of $U$ is less likely since its value is about 6 eV at ambient pressures.

The ZSA framework cannot describe the region near the transition because when $E_{\rm CTG}$ is on the order of other excitations of the solid (e.g., excitons, phonons) all excitations together will ultimately determine the phase diagram. A mean field model proposed by Giesekus and Falicov [10] predicts, for example, the possibility of an *abrupt* closure of $E_{\rm CTG}$ caused by excitonic effects. This suggests that the conspicuous knee in Fig. 3 may be caused by a discontinuity in the resistivity smoothed over by the pressure inhomogeneity. A discontinuous closing would also reconsider the difference between the metallization pressure determined by absorption and resistivity measurements. Further measurements are necessary to determine these fine details of the IM transition.

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[22] One indication that the pressure dependence of the $p$-$d$ hybridization is important is the large increase in the Néel temperature with pressure. Unfortunately there is not sufficient information to estimate the pressure dependence of all the hybridization shifts from just the Néel temperature. One may argue that the ground state hybridization shift, $\delta_0$, is $\sim V_{pd}^2/\Delta$ (where $V_{pd}$ is the $p$-$d$ transfer integral) which has been shown to be $\propto 10Dq$, the octahedral crystal-field splitting [P. W. Anderson, Phys. Rev. **115**, 2 (1959)]. Now $10Dq$ (and thus $\delta_0$) has been shown to scale with volume as $V^{-5/3}$ [H. G. Drickamer, in *Solid State Physics,* edited by H. Ehrenreich *et al.* (Academic, New York, 1964), Vol. 17, p. 1]. A quantitative estimate of the pressure dependences of the other hybridization shifts $\delta_{-1}$ and $\delta_{+1}$ is very difficult. However, they should be comparable in magnitude to that of $\delta_0$, thus making the net $p$-$d$ hybridization contribution to the pressure dependence of the charge-transfer gap in Eq. (1) of the same sign as that of $W$.