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CHARGE-TRANSFER GAP CLOSURE IN TRANSITION-METAL HALIDES UNDER PRESSURE

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ABSTRACT Insulator-to-metal transition induced by pressure has been studied in three transition metal iodides: NiI_2, CoI_2 and FeI_2 using optical absorption and resistivity measurements at room temperature. Comparisons between the results obtained by these two techniques suggested that the closure of the charge-transfer gap is the principal mechanism responsible for the insulator-to-metal transition in these materials.

INTRODUCTION

Mott [1,2] was the first one to proposed the existence of an insulating phase in a solid with an odd number of valence electrons as a result of electron-electron correlation. He pointed out that if the electron wave functions are highly localized on the atomic sites, as in the case of the *d* electrons in the transition metals, the strong onsite Coulomb repulsion (U) produces an effective energy gap to conduction known as the Mott-Hubbard gap [3]. Many transition-metal compounds such as NiO are believed to be examples of Mott insulators [1,2,4]. In 1985 Zaanen, Sawatzky, and Allen (ZSA) [5] proposed a more general model of transport in highly correlated electron system. They pointed out that a large *U* is only a *sufficient* condition for a finite transport gap. In their framework, a second kind of insulators in which the charge-transfer energy (Δ) is the minimum transport gap can also exist. These insulators will be referred to as *charge-transfer insulators*. In many transition-metal compounds Δ is the energy necessary to excite an electron from the anion valence band to the transition-metal *d* band. Sawatzky and Allen [6] concluded from x-ray photoemission experiments that NiO is a charge-transfer insulator rather than a Mott insulator. Similar experiments on the transition-metal dihalides led them to propose that these compounds are also charge-transfer insulators [7].

Mott also pointed out that the electronic wave functions in these insulators may be transformed by pressure or temperature from localized to extended states. As a result such insulator-to-metal (IM) transitions are known as Mott transitions [1,2]. The search for Mott transitions is already extensively documented in the literature [2]. The introduction of a new kind of insulator by ZSA opens the possibility for a new type of IM transition that results from the closure of the charge-transfer gap. To date this type of transition has only been reported [8] in some perovskites of the formula $R\mathrm{NiO_3}$ where R is a rare-earth ion. What changes in the magnetic and optical properties that accompany this type of IM transition are still poorly understood. In this paper we investigate the effect of pressure on the charge-transfer gap in several transition-metal dihalides ($\mathrm{NiI_2}$, $\mathrm{CoI_2}$, and $\mathrm{FeI_2}$, to be referred to as TMI for short) using infrared (IR) absorption spectroscopy and a diamond-anvil high-pressure cell (DAC). By comparing IR-absorption and resistivity measurements in $\mathrm{NiI_2}$ under pressure, we have shown previously that the closure of the charge-transfer gap is the fundamental cause of its IM transition [9]. In the present paper we have extended these measurements further into the longer wavelength IR range. We found evidence for a discontinuous gap closure suggesting that the transition may be first-order in $\mathrm{NiI_2}$. In addition, we have extended these measurements to $\mathrm{CoI_2}$ and $\mathrm{FeI_2}$ and shown that pressure-induced charge-transfer gap closure is important for understanding their IM transition also.

BACKGROUND

Crystal Structure and Electronic Properties of Transition Metal Iodides

$\mathrm{NiI_2}$, $\mathrm{CoI_2}$, and $\mathrm{FeI_2}$ all crystallize in similar hexagonal layered structures [10]. Both $\mathrm{CoI_2}$ and $\mathrm{FeI_2}$ have the $\mathrm{CdI_2}$ structure while $\mathrm{NiI_2}$ crystallizes in the $\mathrm{CdCl_2}$ structure. The $3d$ electrons of their transition-metal ions remain in their elemental $3d^n$ configuration. In the solid a gap forms between the occupied and unoccupied $3d$ states because of the strong electron-electron repulsion U. These electronic states thus do not contribute to conductivity even though they are partially filled. The occupied states are more accurately treated as localized impurity states that are split by the crystal field of their nearest-neighbor iodine ions. The nearest-neighbor crystal field is approximately cubic with a small trigonal distortion [11]. Because their $3d$ shells are partially filled, the transition-metal ions have magnetic moments. In $\mathrm{NiI_2}$, $\mathrm{CoI_2}$, and $\mathrm{FeI_2}$ the $3d$ shells have total spins $S = 1$, $S = 3/2$, and $S = 2$ respectively [12]. The magnetic moments of the ions couple ferromagnetically within the hexagonal planes and antiferromagnetically between the planes. The crystals are antiferromagnetic at low temperatures with Néel temperatures (T_N) of 75 K, 3-12 K, and 10 K [12] respectively. In addition, at lower temperatures the spins in $\mathrm{NiI_2}$ and $\mathrm{CoI_2}$ are known to form helical structures [13].

Although no band structure calculations of the above iodides are available, a one-electron band structure of the isostructural $NiBr_2$ has been reported. It is expected to be qualitatively similar to those of the other halides[14]. In forming the iodides, the transition-metal ions give up their two 4*s* electrons to fill the iodine 5*p* shell resulting in a predominantly ionic bond. These empty 4*s* states form a high-lying conduction band with a bandwidth of about 2 eV, while the iodine 5*p* states comprise a manifold of valence bands about 5 eV wide. The Fermi level lies in between the two. The calculated *p* band width in $NiBr_2$ agrees with the result of a recent photoemission study of NiI_2 [15]. The calculation also showed a narrow band (about 0.5 eV wide) of 3*d* states near the Fermi level. It was pointed out by the authors [14] that their single-particle approach was not expected to be accurate for the localized 3*d* electrons. The one-electron calculation showed the Fermi level lying in the partially filled 3*d* band and hence $NiBr_2$ should be a metal. However, all three TMI are known to be insulators at atmospheric pressure [16]. This discrepancy between the one-electron band theory and experiment is explained by the fact that the 3*d* states are highly correlated. In a many-electron picture the occupied 3*d* states on the transition metal ions are known as the lower Hubbard band. The states in which one electron has been transferred from one transition metal ion to another is known as the upper Hubbard band. The energy gap between them is a measure of the onsite Coulomb repulsion energy *U*. The ambient pressure density-of-states and relative positions of the various bands in the TMIs are shown schematically in Fig. 1. In intrinsic materials *U* inhibits the

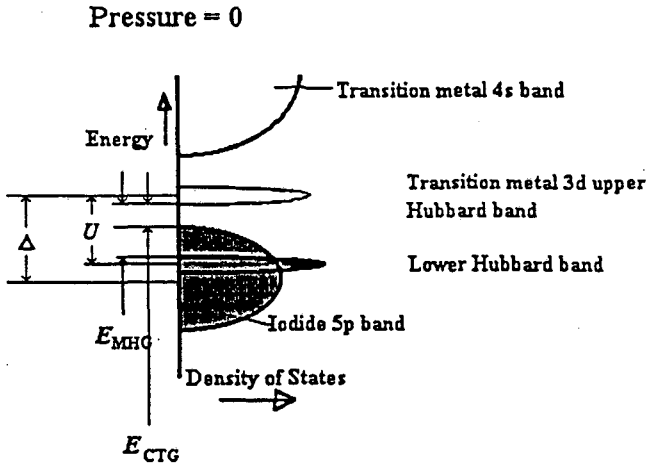


FIG. 1 Schematic density-of-states of TMI at ambient pressure. Δ, *U*, E_{CTG} and E_{MHG} stand, respectively, for the charge-transfer energy, the on-site Coulomb repulsion, the charge-transfer gap and the Mott-Hubbard gap.

hopping of a $3d$ electron from site to site and suppresses conduction. As a result the ground states of the TMIs are insulating.

Zaanen, Sawatzky, and Allen [4] pointed out another path for electronic conduction to occur. Instead of a $3d$ electron hopping from one transition metal ion to another, one can excite an electron from the $5p$ valence band to the $3d$ bands. The energy involved is known as the charge-transfer energy (Δ) since a charge is transferred from an anion to a cation. More formally, U and Δ can be defined as the energies for the following transitions:

$$\Delta: \quad d^n \rightarrow d^{n+1}L$$
$$U: \quad d^n d^n \rightarrow d^{n-1} d^{n+1}$$

where L represents a ligand hole, such as one in the anion valence p band. Following the approach of Mott, we make a clear distinction between the charge-transfer energy and the charge-transfer gap (E_{CTG}) as shown in Fig. 1. If we define B_U, B_L and B_p as the bandwidths of the upper Hubbard band, lower Hubbard band and the anion p band respectively, then E_{CTG} and the Mott-Hubbard gap (E_{MHG}) can be defined as:

$$E_{CTG} = \Delta - (B_U/2) - (B_p/2) . \qquad (1)$$
and $$E_{MHG} = U - (B_U/2) - (B_L/2) . \qquad (2)$$

These energy gaps are also shown in Fig. 1. The relative magnitude of these two gaps determine whether the insulator is a Mott insulator or a charge-transfer insulator.

A number of experiments suggest that the TMI are charge-transfer insulators. From reflectivity studies Pollini et al. [17] identified the lowest energy structures as due to excitons associated with charge-transfer transitions. These peaks are broad (FWHM~0.7 eV) and centered at ~2, 2.5, and 3 eV for NiI_2, CoI_2, and FeI_2 respectively. By adding to these values a $B_p/2$ of about 2.5 eV, we estimate Δ to be in the ranges of 4~5 eV for the TMI. From analysis of the $2p$ x-ray photoemission measurements, Zaanen et al. [7] determined Δ and U in NiI_2 to be 1.5 and 4.5 eV respectively. The values of Δ determined by photoemission and reflectivity experiments are slightly different because photoemission most likely measures E_{CTG} rather than Δ. The identification of the lowest energy structures in the optical spectra with a charge-transfer transition is consistent with the trend observed in the series of Ni dihalides in which the halogen is varied from Cl to I [18,19]. The absorption edges in these dihalides show very large changes in energy from 4 eV in $NiCl_2$ to 1.2 eV in NiI_2 as a result of the decrease in the anion electron affinity. Based on the values of U and Δ they deduced, Zaanen *et.*

al. [7] concluded that NiI_2 is a charge-transfer insulator. However, because of the large uncertainties in the determination of Δ, U, E_{CTG} and E_{MHG} their conclusion is not generally accepted.

Pressure-induced IM Transition in Transition Metal Iodides

So far pressure-induced IM transition in NiI_2 has been studied in great details by a number of techniques. Pasternak et al. [20] have shown via electrical measurement that NiI_2 exhibited an IM transition at a pressure of about 19 GPa. Mössbauer spectroscopy indicated an antiferromagnetic to diamagnetic transition due to disappearance of the Ni magnetic moments accompanied this transformation while no structural change was found by x-ray. These findings are consistent with both closure in U or Δ. More recently, we have studied the pressure dependence of near-infrared absorption in NiI_2 [9]. We concluded that its IM transition was driven by the closure of the charge-transfer gap. Some of these measurements in NiI_2 have also been extended to CoI_2. For example, Mössbauer spectroscopy has shown the disappearance of the Co magnetic moment at 13 GPa [21]. However, the situation in CoI_2 is complicated by the appearance, at around 9 GPa, of a nonmagnetic phase which coexisted with the antiferromagnetic phase. Electrical measurements on CoI_2 indicated the onset of a IM transition around 9 GPa [22]. As far we know no pressure dependent x-ray measurements have been reported on CoI_2. Thus the existing data indicated that a pressure-induced IM transition is a common feature of the TMI. Optical measurements suggest that this transition is driven by the closure of the charge-transfer gap in NiI_2. However, whether this is also true for other TMI' is not known. The purpose of the present work is to extend the optical measurements in NiI_2 to the iodides of Co and Fe.

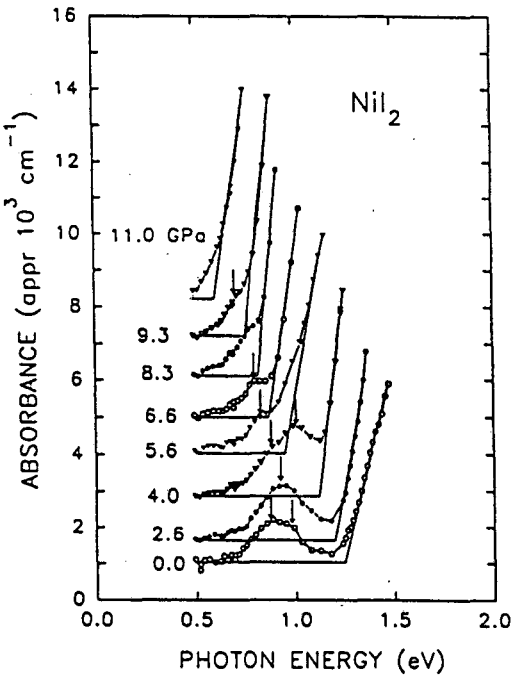
EXPERIMENTAL DETAILS AND RESULTS

The TMI compounds used in our experiments were high purity, fine grain powders obtained from Alfa Products. Single crystals were grown by the vapor transport method inside an evacuated quartz ampoule using a three-zone furnace. Since TMI (especially FeI_2) are quite hygroscopic care was taken to minimize the exposure of the starting TMI powder to air. The quartz tube was heated to 150°C for several hours to drive off any residual water and sealed with a hydrogen/oxygen torch. NiI_2, CoI_2, and FeI_2 were grown at temperatures of 700-730°C, 480-500°C, 480-500°C respectively for a period of about 150 hours. The higher (lower) figure indicates the temperature at the powder (growth) end of the ampoule. The resulting platelets were about 1 cm in diameter.

The high pressure diamond-anvil cell (DAC) used in our experiment has been described before [23] and therefore will not be repeated here. Two kinds of experiments have been performed on samples inside the DAC: near IR absorption

and resistivity measurements. The latter was used as a monitor of the IM transition. As a result of their layered structure the samples can be easily cleaved perpendicular to the *c-axis* into thin sheets of about 10 μm thick. These are further cut into sizes of about 50x50 μm^2. $CaSO_4$ powder was used as the pressure medium in electrical measurements resulting in a pressure inhomogeneity of typically about ±8%. Four contacts were made to the samples with 0.5 mil gold wires. Resistivities were estimated from sample dimensions. Only room temperature resistivity versus pressure results will be presented here. Resistivity measured in NiI_2 as a function of temperature at constant pressure has already been reported in Ref. 9.

Liquid nitrogen was used as the pressure medium in the absorption experiments. The pressure inhomogeneity is estimated to be about ±3% in this case. The experimental setup for photon energies above 0.5 eV has been described in Ref. 24 already. In this paper we have extended the IR absorption measurements on NiI_2 to 0.3 eV using a Digilab Fourier-transform spectrometer. These measurements were performed in a small Merrill-Bassett type DAC at liquid helium temperature with a detector located directly behind the DAC and maintained at the same temperature.



For completeness the room temperature optical absorption spectra of NiI_2 as a function of pressure are reproduce in Fig. 2 although they can been found also in Ref. 9. Figure 3 and 4 shows the corresponding spectra for CoI_2 and FeI_2. Figure 5 shows the low temperature IR absorption spectra in NiI_2 for photon energies between 0.3 and 0.55 eV at three different pressures.

FIG. 2 Room temperature optical absorption spectra of NiI_2 at various pressures. The spectra have been displaced vertically for clarity.

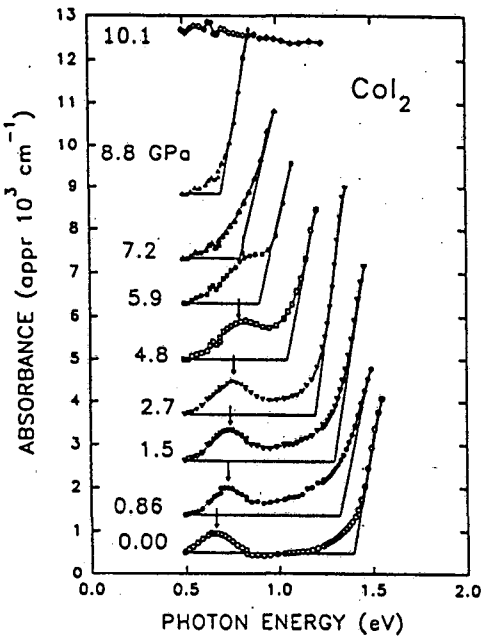


FIG. 3 Room temperature optical absorption spectra of CoI_2 at various pressures. The spectra have been displaced vertically for clarity.

Following previous workers we interpret the spectra in Figs. 2-4 as composed of two kinds of transitions: the weak and broad peaks at low energy are due to intra-*d* transitions of the transition metal ions while the strong and steeply rising edges are due to charge-transfer transitions between the *p* valence bands and empty *d* bands. By extrapolating the charge-transfer edge to zero absorption we determine the energy of the charge-transfer gap (E_{CTG}) as a function of pressure. The results for CoI_2, and FeI_2 are shown in Fig. 6 while those for NiI_2 can be found in Ref. 9. By fitting the experimental points with a straight line we determine the pressure coefficients dE_{CTG}/dP and P_0, the pressures at which E_{CTG} extrapolates to zero, for NiI_2, CoI_2, and FeI_2. The resultant values are listed in Table 1.

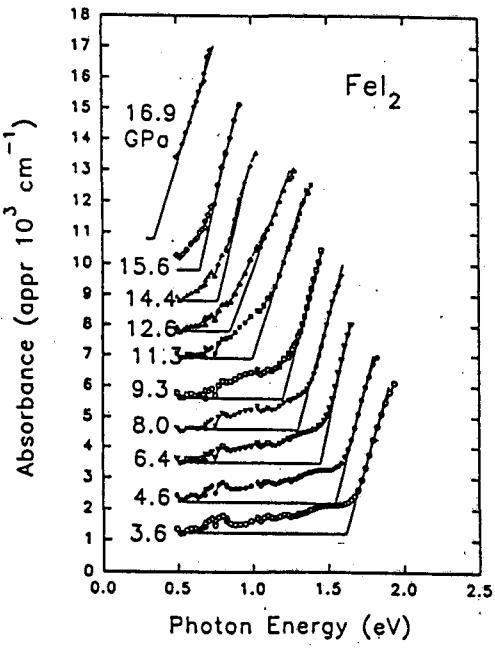
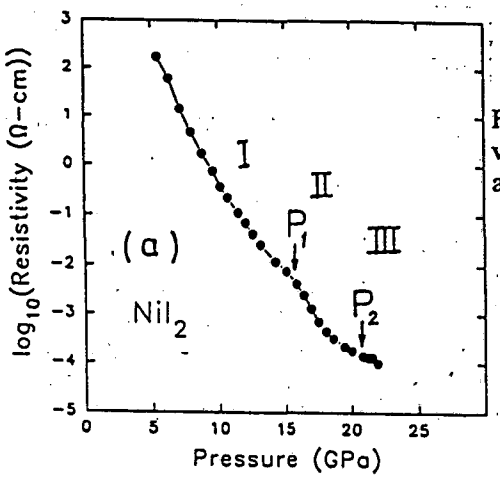


FIG. 4 Room temperature optical absorption spectra of FeI_2 at various pressures. The spectra have been displaced vertically for clarity.



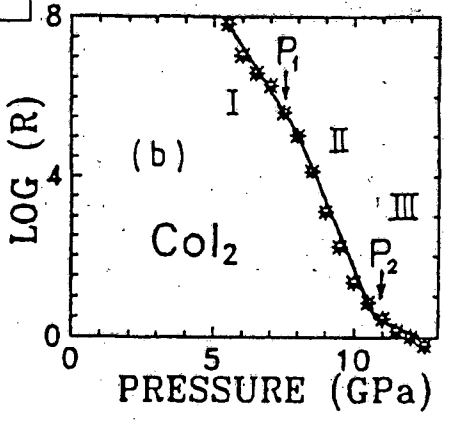
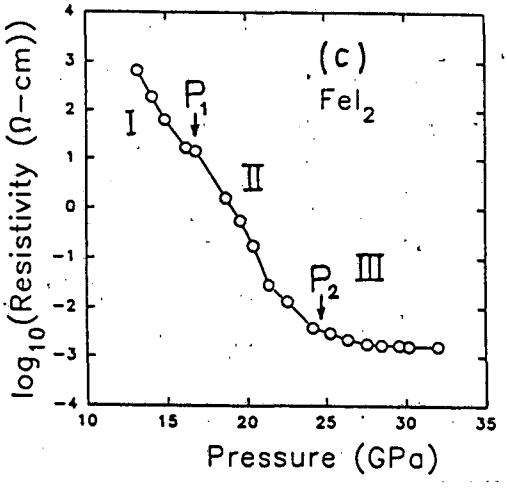


FIG. 7 Room temperature resistivity versus pressure in (a) NiI_2, (b) CoI_2, and (c) FeI_2.

Hubbard bands to be the underlying mechanism. The predicted phase diagrams depend strongly on whether *p-d* hybridization is included. Using a mean-field approximation and neglecting *p-d* hybridization, Freericks and Falicov [25] found a first-order phase transition between an antiferromagnetic insulating state and a diamagnetic metallic state at T>0.



They also predicted the disappearance of the transition metal ion magnetic moments and the IM transition to occur simultaneously before Δ vanished. These results are in qualitative agreement with our results. When *p-d* hybridization was included, Giesekus and Falicov [26] found that at T=0 the phase diagrams might contain a first-order IM transition only, two second-order transitions, or both first and second-order phase transitions depending on the strength of the *p-d* interaction. Thus it is not possible to make quantitative

comparison between theory and experiment without a means to relate pressure to *p-d* hybridization.

To understand this relation, we will now consider the pressure dependence of the charge-transfer gap E_{CTG}. According to Eq. (1), which does not include *p-d* hybridization, E_{CTG} is related to the charge-transfer energy, Δ, and the bandwidths B_U and B_p of the upper Hubbard band and the anion 5*p* valence band respectively. Since $B_U << B_p$ we shall neglect it from now on. When *p-d* hybridization is included, we have to add to Eq. (1) the hybridization energies δ_0, δ_{-1} and δ_{+1}. Briefly these represent, respectively, the changes in the energies of the d^n, d^{n-1} and d^{n+1} electron states (n=8, 7, and 6 ,respectively, for the Ni^{2+}, Co^{2+} and Fe^{2+} ions) as a result of hybridization. Thus Eq. (1) is changed to:

$$E_{CTG} = \Delta - (B_p/2) + 2\delta_0 - \delta_{-1} - \delta_{+1} \qquad (3)$$

As pointed out in Ref. 9, the charge transfer gap involves quantities such as the Madelung energy which are not too sensitive to volume changes. The most important contributions to dE_{CTG}/dP comes from the pressure dependence of B_p. However, in NiI_2 this contribution accounted for only about 60% of dE_{CTG}/dP. The remaining 40% must come mainly from the pressure dependence of the hybridization energies. It is difficult to estimate quantitatively their pressure coefficients. Qualitatively, we expect δ_{+1} to be the smallest of the three and probably can be neglected. Both δ_0 and δ_{-1} are dependent on the *p-d* hybridization matrix element squared: T. Assuming that T is small compared to the separations between the ground state and excited states, one can argue from perturbation theory that the hybridization energies depend on T divided by these energy separations. For δ_0 this energy denomination is just Δ while for δ_{-1} it is equal to U-Δ [5]. For the TMI U and Δ are not too different, therefore we expect that δ_{-1} to be larger than $2\delta_0$. As a result the overall effect of the hybridization energies in Eq. (3) is to decrease the charge-transfer gap just like B_p. In addition we expect the hybridization energies to increase as the distance between the atoms are reduced by pressure. Hence the pressure coefficients of the hybridization energies have the same sign as that of dB_p/dP. Thus our results suggest that the *p-d hybridization energies in the TMI increases with pressure at the rate of around tens of meV/GPa*. This rather large pressure coefficient is consistent with the strong increase in the Néel temperatures with pressure as observed in both NiI_2 and CoI_2 by Mössbauer effect [20,21]. An increase in the *p-d* hybridization will lead to a stronger super-exchange between the transition metal ions and hence to a higher Néel temperature. One may argue that a strong pressure dependence in *p-d* hybridization is not consistent with the insensitivity of the isomer shift to pressure observed by Mössbauer effect [20,21]. We should point out that the isomer shift is most sensitive to the electron charge density at the halide nuclei. Since both the *p*

and *d* electrons have very small wave functions at the origin, actually a rather large change in the hybridization is necessary to produce even the small observed increase in isomer shift with pressure.

CONCLUSIONS

We have studied the closure of the charge-transfer gap in three transition metal di-iodides under pressure by optical measurements. The optical results are found to correlate well with resistivity measurements in showing that the IM transition is driven by the closure of the charge-transfer gap. However, detailed optical and resistivity measurements also showed that the metal phases first appeared before the closure of this gap. The pressure dependence of the charge-transfer gap pointed towards a strong increase in the *p-d* hybridization under pressure.

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