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Title: **High Pressure Metallization of Mott Insulators: Magnetic, Structural and Electronic Properties**

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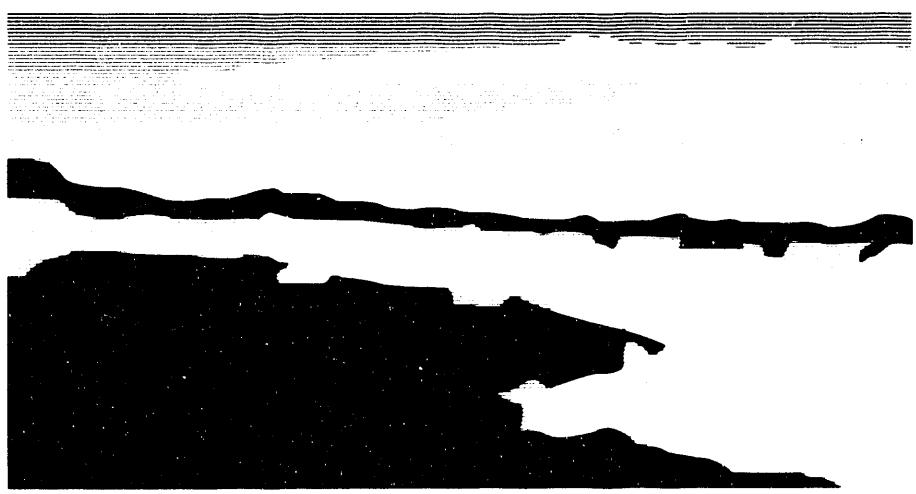

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HIGH PRESSURE METALLIZATION OF MOTT INSULATORS; MAGNETIC, STRUCTURAL AND ELECTRONIC PROPERTIES

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The discovery of high-temperature superconductors in doped Cu-oxides has renewed the interest in one of the oldest fundamental (and still unsolved problems) in condensed matter physics, namely, the metal-insulator transition in the so called Mott Insulators (MI). Most of 3d transition-metal (TM) compounds, (particularly the binary ones) are MI, characterized by very narrow 3d bands where electron-electron interaction is strong. Thus the electron correlation effects are predominant, leading to the breakdown of the simplistic one-electron band theory.

Metallic conductivity in MI can be achieved in two ways, namely, via valence changes and band-gap closure. In the first procedure the mean valence of the TM ions are shifted from an integral to intermediate values by chemical substitution or stoichiometry control. This leads to doping of extra electron or hole carriers. However, in contrast to classical semiconductors, chemical substitution of narrow band insulators also results in severe electronic and structural disorder in the MI under study. The second procedure, the band-gap closure, is achieved by reducing the splitting between energy bands and/or increasing the bandwidth. Due to relatively large band gap energies characteristic to most MI, this is possible only by applying external pressure.

In this article we address the pressure-induced Mott Transition (MT) into a metallic state by the gap-closure mechanism. The band gap of the MI can be classified into two main types: (i) the d-d Mott-Hubbard[3] (intra-band gap) involving the d-d Coulomb repulsive energy U, or (ii) of the ligand-p to metal-d charge-transfer (CT) type (inter-band gap). The materials studied were representative of the structurally isomorphous $(TM)I_2$ (TM=V,Fe,Co and Ni) compounds. They consist of alternating layers of weakly interacting I-TM-I slabs and are antiferromagnetic with T_N of 15, 10, 12

and 75K corresponding to V, Fe, Co and Ni, respectively. The TM cation sublattice moments are coupled ferromagnetically.

As suggested by Zaanen et al. [Phys. Rev. Lett. 55, 418 (1985)], VI2 represents a typical case of a pure Mott-Hubbard type insulators whereas the Fe, Co, Ni diiodes are of the CT type. High pressure studies of the electronic, magnetic and structural properties of the $(TM)I_2$ were carried out in the insulator and the metallic pressure ranges. The experimental tools used were: Resistivity, ^{57}Fe and ^{129}I Mossbauer Spectroscopy (MS), and X-ray diffraction (XRD) using diamond anvil cells (DAC) to provide unique information for characterizing the magnetic and electronic properties of the MI and the nature of the MT. It was shown that, (i) the pressure at which the insulator-metal transitions occur (Pc) coincides precisely with that of the loss of magnetism and (ii) the d-bands remain extremely narrow up to the highest pressure applied.

HIGH PRESSURE METALLIZATION OF MOTT INSULATORS; MAGNETIC, STRUCTURAL AND ELECTRONIC PROPERTIES*

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High pressure studies of the *insulator-metal* transition in the $(TM)I_2$ (TM = V, Fe, Co and Ni) compounds are described. Those divalent transition-metal iodides are structurally isomorphous and classified as *Mott Insulators*. Resistivity, X-ray diffraction and Mössbauer Spectroscopy were employed to investigate the electronic, structural, and magnetic properties as a function of pressure both on the highly correlated and on the metallic regimes.

INTRODUCTION

The discovery of high-temperature superconductors in doped Cu-oxides renewed the interest in one of the oldest fundamental and still unsolved problems in condensed matter physics, namely, the **metal-insulator transition** in the so called *Mott Insulators* (MI)[1]. Most of 3*d* transition-metal (TM) compounds, (particularly the binary ones) are MI, characterized by very narrow 3*d* bands where electron-electron interaction is strong. Thus the electron correlation effects are predominant, leading to the breakdown of the simplistic one-electron band theory.

Metallic conductivity in MI can be achieved in two ways, namely, via *valence changes* and *band-gap closure*. In the first procedure the mean valence of the TM ions are shifted from an integral to intermediate values by chemical substitution or stoichiometry control. This leads to *doping* of extra electron or hole carriers. However, in contrast to classical semiconductors, chemical substitution of narrow band insulators also results in severe electronic and structural disorder in the MI under study. The second procedure, the band-gap closure, is achieved by reducing the splitting between energy bands and/or increasing the bandwidth. Due to relatively large band gap energies characteristic to most MI, this is possible only by applying external pressure[2].

In this article we address the pressure-induced *Mott transition* (MT) into a metallic state by the gap-closure mechanism. The band gap of the MI can be classified into two main types: (*i*) the *d-d* Mott-Hubbard[3] (intra band gap) involving the *d-d* Coulomb repulsive energy *U* or (*ii*) of the ligand-*p* to metal-*d* charge-transfer (CT) type (inter band gap), involving the $d_i^n \rightarrow d_i^{n+1}L$ energy Δ, where L denotes a hole in the anion valence band[4]. The materials studied were representative of the structurally isomorphous $(TM)I_2$ (TM = V, Fe, Co and Ni) compounds with their closely related space groups *R*3*m* or *C*3*m*. They consist of alternating layers of weakly interacting *I-TM-I* slabs and are antiferromagnetic with T_N of 15, 10, 12 and 75K corresponding to V, Fe, Co and Ni, respectively. The TM cation sublattice moments are coupled ferromagnetically.

As suggested by Zaanen et al.(Ref. 4), VI_2 represents a typical case of a pure Mott-Hubbard type in-

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sulators whereas the Fe, Co, Ni diiodides are of the CT type. High pressure studies of the electronic, magnetic and structural properties of the $(TM)I_2$ were carried out in the insulator and the metallic pressure ranges. The experimental tools used were: Resistivity, ^{57}Fe and ^{129}I Mössbauer Spectroscopy (MS), and X-ray diffraction (XRD) using diamond anvil cells (DAC).

EXPERIMENTAL

Samples Preparation

Samples were synthesized from the direct solid-vapor reaction of the elements taking place in an evacuated quartz tube heated to 700 °C. The MS samples were prepared from enriched isotopes of ^{57}Fe and ^{129}I. All the $(TM)I_2$ are highly hygroscopic and special precautions were taken when loading into the DAC's.

Measurements

The DAC's used in the present experiments were the Merrill-Bassett triangular-type[5] or related miniature-type[6]. The ruby fluorescence method[5] was used for manometry. The pressure and temperature ranges covered were 0 - 50 GPa and 4 - 350 K respectively.

Resistivity measurements were performed using the quasi - four point method with 10-μm thick gold electrodes. At pressures close to the metal-insulator transition (P_c) the temperature dependence of $R(P)$ was obtained. P_c was determined as the pressure at which the slope of $R(T)$ became positive, namely the material became metallic.

Mössbauer Spectroscopy was carried out using the 27.8-keV ^{129}I resonance in all $(TM)I_2$ and the 14.4-keV ^{57}Fe resonance in FeI_2. A $Ta_{0.90}W_{0.10}$ gasket/collimator was used and samples diammeters were in the 300 - 800-μm range. A detailed description of the ^{129}I MS is found in Ref. 7. For the $^{57}FeI_2$ MS measurements a commercial 5-mCi $^{57}Co(Rh)$ *point* source of 0.5x0.5 mm dimension was used[8]. At each pressure data were collected as a function of temperature from which we determine the pressure dependence of T_N, the hyperfine field H, Quadrupole Splitting QS and Isomer Shift IS. At $T>T_N$ the Mössbauer spectra were determined solely by the quadrupole interaction whereas at $T<T_N$ by the combined magnetic and quadrupole interactions. For a polycrystalline sample with randomly oriented crystallographic and magnetic axes with respect to the direction of the γ-ray the *Spin-Hamiltonian -H-* governing the hyperfine interaction can be expressed as:

$$H = \mu H (\hat{I}_z/I) + \{e^2q_{zz}Q (3\cos^2\theta - 1)/[8I(2I-1)]\}\cdot\{3\hat{I}_z^2 - I(I-1)\} \quad (1)$$

where μ is the nuclear moment, $\hat{I}_z$ and $\hat{I}_z^2$ are spin operators and eq_{zz} is the principal axis of the electric-field-gradient (*efg*). In the $(TM)I_2$ the *efg* along the c-axis and is axially symmetric. For each spectrum the MS parameters, namely, H, $e^2q_{zz}Q$, θ and the IS were determined from the experimental points using an appropriate least-squares fitting program. At each pressure the temperature dependence of H allows the measurement of T_N, the temperature at which $H \to 0$.

XRD patterns were collected at 300 K using a Guinier spectrometer. Main emphasis was at pressures near P_C in order to detect and characterize possible crystallographic phase transitions. In all cases no structural changes were observed at the *insulator-metal* pressure transition.

RESULTS and DISCUSSION

Magnetism in the Mott Insulator Phase.

Any magnetic insulator, a material whose local moments and energy gap persist above the spin ordering temperature, can be classified as a Mott insulator, and *vice versa*. As long as the 3*d*-bands are well localized one would expect an increase in T_N and no variation in the local moments with increasing pressure. The first experimental proof for this statement

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was provided by Pasternak et al. in the case of NiI_2 (Ref. 9).

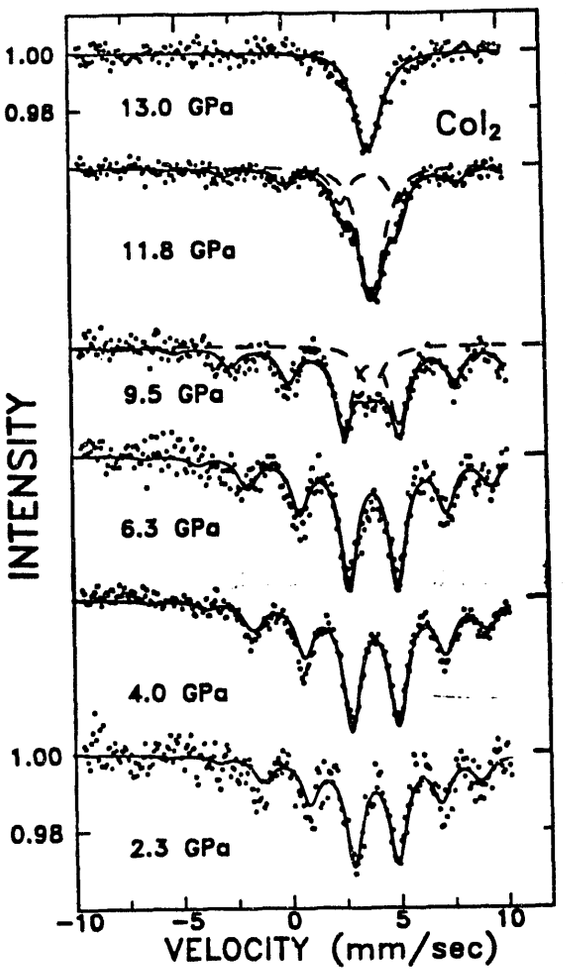

Fig.1 Typical Mössbauer spectra of CoI_2 at 4 K recorded at several pressures. The solid line is a theoretical curve obtained by least-squared fitting to the experimental points. The source is $Mg_3{}^{129m}TeO_6$.

The pressure variation of the ^{129}I hyperfine field H in CoI_2 at 4 K ($T \ll T_N$) is shown in Fig. 1. The hyperfine field at low T is proportional to the Co^{2+} moment. As can be seen, the field at 13 GPa has collapsed. Within the 0 - 13 GPa pressure range the MI regime persists. The variation in pressure of T_N, H and IS is shown in Fig. 2. New data on H(P) and T_N(P) as measured with ^{57}Fe in FeI_2 are shown in Fig. 3.

The Mott Transition.

The concurrence of an isostructural insulator-metal transition and of *d*-electron delocalization are inherent features of a MT. The insulator-metal transition is uniquely determined by resistivity measurements[10]. The pressure variation of $\log(R)$ for CoI_2 is shown in Fig. 3. One clearly sees the dramatic decrease of R with increasing P (by seven orders of magnitude) leveling off at P > 12 GPa. As mentioned before, P_c is determined from $R(T)$ measurements.

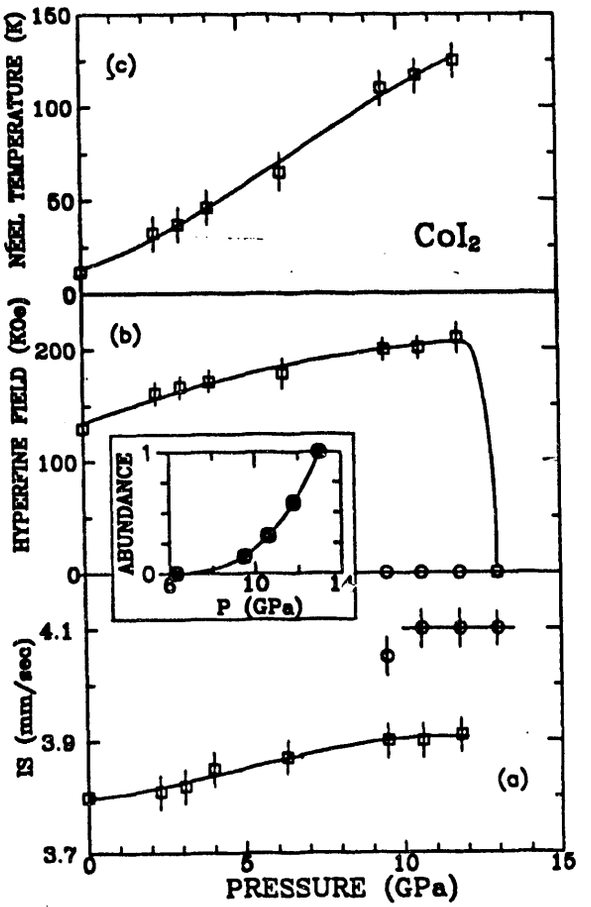

Fig. 2 Pressure dependence of the IS (a), H (b) and T_N (c) of CoI_2. The insert shows the pressure dependence of the abundance of the metallic state. Note the jump in IS due to the MT.

The effect of gap band closure, the MT, on the magnetic properties of the MI is to effectively cancel the local moments. This is indeed observed in the MS studies. The case of CoI_2 is quite unique

unlike NiI_2. Within $7 < P < 13$ GPa one observes the coexistence of insulating (correlated) and metallic states; the abundance of the latter increases with increasing P, reaching unity at ≈ 13 GPa (insert in Fig. 2). This phenomena is not detected by the Resistivity measurements. Within this pressure range the R(T) slope is *positive* indicating a metallic regime and yet R(P) decreases in value! The nature of the metallic behavior is due to the **percolative** mechanism. A complete transition into the non-magnetic state is rather sharp, providing a well defined and more reliable method for determining P_c. Values of P_c for the V, Co and Ni are 44, 13 and 19 GPa, respectively. P_c of FeI_2 has not yet been determined, but it is greater than 29 GPa.

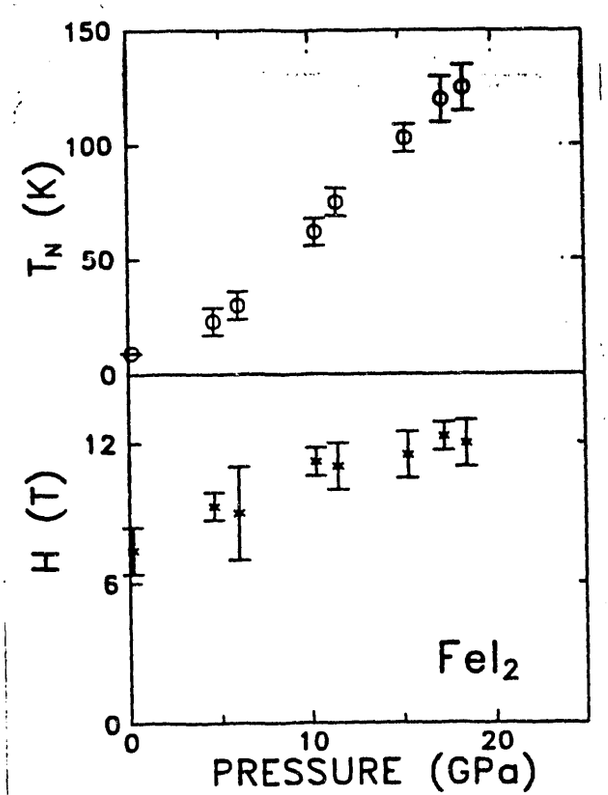

Fig.3 The pressure dependence of H and T_N in $^{57}FeI_2$ in the pressure range of 0 - 19 GPa.

According to Zaanen et al.[4] the CT mechanism dominates the "heavy" transition metal compounds. However there is no way *a priori* to predict the nature of the gap-closure at those high pressures. The ^{129}I MS provides an unique tool through the IS for assessing the nature of the MT. The *inter-band* closure which causes the I^- 5*p*-band population to decrease, concomitantly transferring electrons into the empty 3*d* band; this will directly affect the IS. It has been shown that the ^{129}I IS behaves linearly[11] with the number of 5*p*-holes (h_p) (with respect to a Mg_3TeO_6 source)[12]:

$$IS = 1.27\ h_p + 3.6\ (mm/s) \qquad (2)$$

In case of NiI_2 (Ref. 9) no abrupt change is observed in IS(P) at and around P_c, whereas the IS of metallic CoI_2 increases abruptly by 0.20 mm/s (see Fig. 4) corresponding to 0.16 h_p per ligand. Thus according to the ^{129}I MS data the NiI_2 MT is of a Mott-Hubbard type (intra-band) whereas that of CoI_2 is of the CT (inter-band). Experiments are now underway to determine the Mott character of VI_2, MnI_2 and FeI_2.

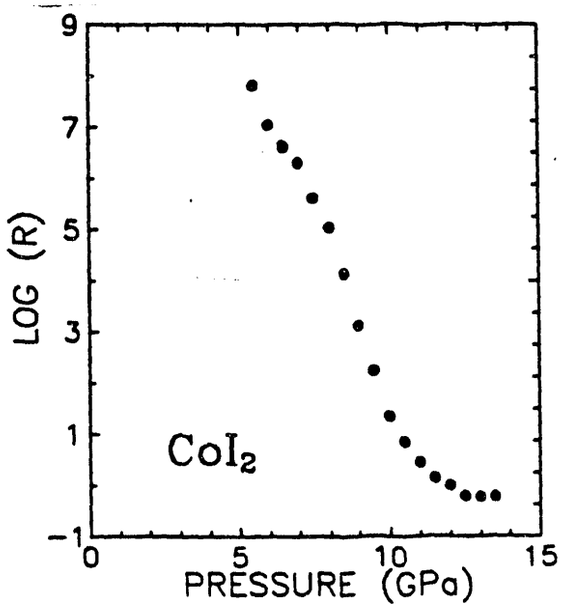

Fig. 4 Pressure dependence of the Resistance of CoI_2 measured at 300 K. The curve levels off near P_c.

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CONCLUSIONS

The combined XRD, MS and Resistivity methods used in conjunction with DACs have been shown to provide unique information for characterizing the magnetic and electronic properties of the MI and the nature of the MT. It was shown that, (*i*) the pressure at which the *insulator-metal* transitions occur (P_c) coincides precisely with that of the loss of magnetism and (*ii*) the *d*-bands remain extremely narrow up to the highest pressure applied. This last observation is in accordance to the recent findings[2] in the $RNiO_3$ where CT transitions were observed at ambient pressure with change of temperature alone.

REFERENCES

*** Supported in part by grants from the DOE-IGPP and** the Israeli Basic Research Foundation.

1 - N.F Mott, *Proc. Phys. Soc.* London, **A62**, 416, 1949; G.A. Sawatzky, in *Earlier and Recent Aspects of Superconductivity*, Eds..G. Bednorz and K.A. Müller, Heidelberg: Springer-Verlag Berlin pp. 345-376, 1990; N. Tsuda, K. Nasu, A. Yanase and K. Siratori, *Electronic Conduction in Solids*, Springer-Verlag, Berlin, 1991.

2 - An exceptional case where gap closure was obtained by temperature increase at ambient pressure are some of the rare-earth nickelate perovskites, see J.B. Torrance et al. *Phys Rev.* **B45**, 8209, 1992.

3 - J. Hubbard, *Proc. Roy. Soc.* London **A277**, 237, 1964; *ibid.* **A281**, 401, 1964.

4 - J. Zaanen, G.A. Sawatzky and J.W. Allen, *Phys. Rev. Lett.* **55**, 418, 1985.

5 - A. Jayaraman, *Rev. Mod. Phys.* **55**, 65, 1983.

6 - E. Sterer, M.P. Pasternak and R.D. Taylor, *Rev. Sci. Instrum.* **71**, 1117, 1990.

7 - M.P. Pasternak and R.D. Taylor, *Hyperfine Interact.* **47**, 415, 1989; *ibid.* **53**, 159, 1990.

8 - G.R. Hearne, M.P. Pasternak and R.D. Taylor, *Hyperfine Interact.*, to be published.

Begin here

9 - M.P. Pasternak, R.D. Taylor, A. Chen, C. Meade, L.M. Falicov, A. Giesekus, R. Jeanloz and P.Y. Yu, *Phys. Rev. Lett.* **65**, 790, 1990.

10 - The gap closure of the CT-type MI can in principle be determined by optical spectroscopy. However, the evolution of low energy gap semiconductors at pressures below P_c may be misleading, inferring a metallic state to an actual gapped state.

11 - S.L. Ruby and G.K. Shenoy, *Mössbauer Isomer Shifts*, G.K. Shenoy and F.E. Wagner eds.,Amsterdam: North Holland, 1978, p 617.

12 - M. Van der Heyden, M.P. Pasternak and G. Langouche, *J. Phys. Chem. Solids* **46**, 1221, 1985.

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