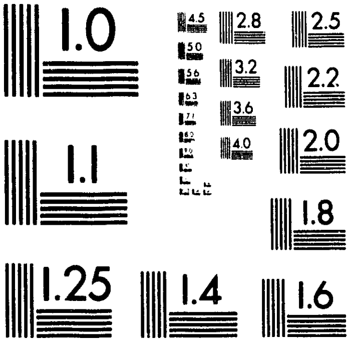
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Title: **Pressure Induced Metallization of the Mott Insulator VI_2***

*Vanadium diiodide

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PRESSURE INDUCED METALLIZATION OF THE MOTT INSULATOR VI_2

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The majority of the binary Transition-Metal (TM) compounds exhibit the fundamental phenomenology of Mott Insulators, namely, (i) they are antiferromagnetic insulators in which local moments persist unchanged above T_N, (ii) they have relatively large optical band gaps and (iii) excitons are present in their optical absorption spectrum. Among numerous binary Mott Insulators (MI) TM diiodides (TM=V,Cr, MN, Fe, Co and Ni) constitute an interesting case for studying pressure-tuned electronic and magnetic properties.

The $(TM)I_2$ are structurally isomorphous and are all antiferromagnetic with the TM cations forming a ferromagnetic ordered layer separated by two adjacent iodine layers. The present study deals with the lightest of the TM diiodides, VI_2, an antiferromagnetic (T_N=15K) insulator. Measurements were carried out to determine the Insulator-Metal transition using Resistivity and ^{129}I Mossbauer Spectroscopy methods.

Vanadium diiodide crystallizes with a CdI_2 structure in which the TM is surrounded by a nearly octahedral environment of six iodine ions, whereas each iodine is bound to three equivalent nearest neighbor metal ions. The spin direction in the antiferromagnetic state has been determined by Mossbauer Spectroscopy and found to be along the V-I bond direction (54 degrees with respect to the c-axis).

Using diamond anvil cells, ^{129}I Mossbauer Spectroscopy (MS) and Resistivity measurements were carried out in VI_2 as a function of pressure (O<P<45 GPa) and temperature (4<T<300K). MS to 15 GPa reveals an impressive increase in the Neel temperature and a slight increase in the Transferred Hyperfine Field. The pressure behavior of R(P,T) in particular near the metal-insulator pressure P_c=44 GPa, is described. Being he lightest transition metal (TM) in the isostructural $(TM)I_2$ series of the iodides compounds, the V^{2+} (d^3 configuration) represents a typical candidate for a pure Mott-Hubbard gap closure. Results are compared with the heavy TM diiodides such as NiI_2 and CoI_2 where it is expected that the Charge Transfer regime prevails.

PRESSURE INDUCED METALLIZATION OF THE MOTT INSULATOR VI_2*

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Using diamond anvil cells, ^{129}I Mössbauer Spectroscopy (MS) and Resistivity measurements were carried out in the layered antiferromagnet VI_2 as a function of pressure ($0<P<45$ GPa) and temperature ($4<T<300K$). MS to 15 GPa reveals an impressive increase in the *Néel temperature* and a slight increase in the *Transferred Hyperfine Field*. The pressure behavior of R(P,T), in particular near the metal-insulator pressure P_c=44 GPa, is described. Being the lightest transition metal (TM) in the isostructural $(TM)I_2$ series of the iodides compounds, the V^{2+} (d^3 configuration) represents a typical candidate for a pure **Mott-Hubbard** gap closure. Results are compared with the *heavy* TM diiodides such as NiI_2 and CoI_2 where it is expected that the **Charge Transfer** regime prevails.

INTRODUCTION

The majority of the binary Transition-Metal (TM) compounds obey the fundamental phenomenology of *Mott Insulators*[1] namely, (*i*) they are antiferromagnetic insulators in which local moments persist unchanged above T_N, (*ii*) they have relatively large optical band gaps and (*iii*) excitons are present in their optical absorption spectrum. Among numerous binary *Mott Insulators* (MI) TM diiodides (TM = V, Cr, Mn, Fe, Co and Ni), as will be discussed later, constitute an interesting case for studying pressure-tuned electronic and magnetic properties.

The $(TM)I_2$ are structurally isomorphous and are all antiferromagnetic with the TM cations forming a ferromagnetic ordered layer separated by two adjacent iodine layers. The present studies deal with the lightest among the TM diiodides; VI_2, an antiferromagnetic (T_N=15K) insulator. Measurements were carried out to determine the *Insulator-Metal* transition using Resistivity and ^{129}I Mössbauer Spectroscopy methods[2]. Of the latter, only preliminary findings will be reported.

Vanadium diiodide crystallizes with a CdI_2 structure (space group $C\bar{3}m$) in which the TM is surrounded by a nearly octahedral environment of six iodine ions, whereas each iodine is bound to three equivalent nearest neighbor metal ions. The spin direction in the antiferromagnetic state has been determined by Mössbauer Spectroscopy (Friedt et al.[3]) and found to be along the V-I bond direction; 54 degrees with respect to the *c*-axis.

EXPERIMENTAL

Sample Preparation

Samples in milligram amounts were prepared by direct solid-vapor reaction of high purity vanadium metal and elemental iodine. For the R(P,T) measurements, iodine in its natural abundance form was used. For MS measurements an absorber was prepared using $Pd^{129}I_2$ which decomposes to I_2 at 350 ^{0}C. Stoichiometric amounts of the elements were encapsulated under vacuum in a quartz tube and heated for 24 hours at 850 ^{0}C. The purple/pink VI_2 crystals were loaded under dry atmosphere inside a glove box.

Measurements

Mössbauer Spectroscopy spectra were recorded using a top-loaded variable temperature He cryostat. in conjunction with a $Mg_3{}^{129m}TeO_6$ source. A Merill-Bassett cell with $Ta_{0.9}W_{0.1}$ gasket alloy was used. Pressures[2] were determined by the ruby fluorescence method.

Resistivity measurements were carried out in a miniature Diamond Anvil Cell[4] (DAC) using a quasi four-point method. Gold wire electrodes, 10 μm diameter were applied to the culet of the diamond (400 μm diameter) facing the insulating layer. Up to pressures close to the Mott transition pressure (P_c), measurements were carried out solely at room temperature. At P ~ P_c series of R(P,T) measurements were carried out.

RESULTS

Mössbauer Spectroscopy

Mössbauer Spectroscopy measurements were carried out to P = 15 GPa as function of pressure and temperature. Typical spectra recorded in the antiferromagnetic (4 K) and paramagnetic states (300 K) are shown in Fig. 1. The RT spectrum was fitted with a pure quadrupole splitting and the data at 4 K. with a magnetic and quadrupole interaction assuming the following *Hamiltonian*:

$$H = \mu \mathrm{H}_{eff} I_z + \left\{ \frac{e^2 q_{zz} Q \, (3\cos\theta^2 - 1)}{8I(2I-1)} \right\} \left\{ 3I_z^2 - I(I-1) \right\}$$

where H_{eff} is the hyperfine field at the nucleus, $e^2 q_{zz} Q$ is the quadrupole coupling and θ the angle between H_{eff} and the electric field gradient eq_{zz}

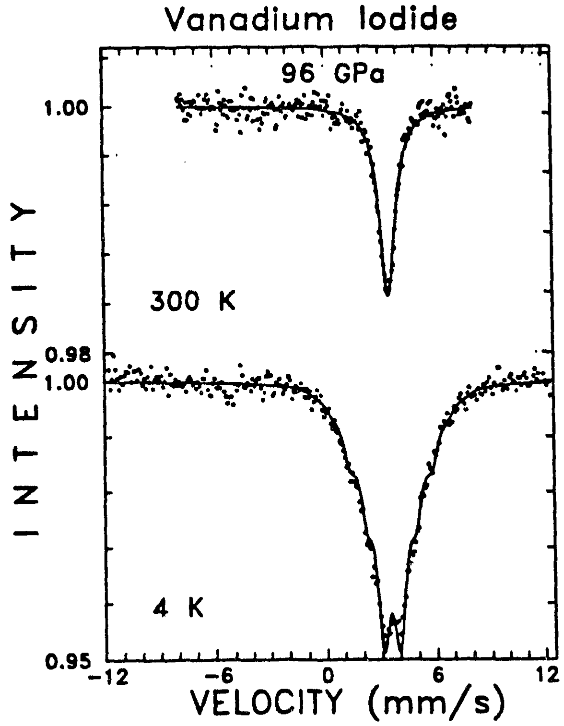

Figure 1. ^{129}I Mössbauer spectrum of VI_2 at 9.6 GPa recorded in the antiferromagnetic (4 K) and in the paramagnetic states (300 K) respectively. The solid line is a theoretical spectrum obtained from least-squares-fitting to the experimental points. The source was $Mg_3{}^{129m}TeO_6$.

Resistivity

The pressure dependence at 300 K of the sample resistance as a function of pressure is shown in Fig. 2. The log(*R*) levels off around 35-40 GPa and does not reach a plateau as would be expected if the whole sample metallizes.

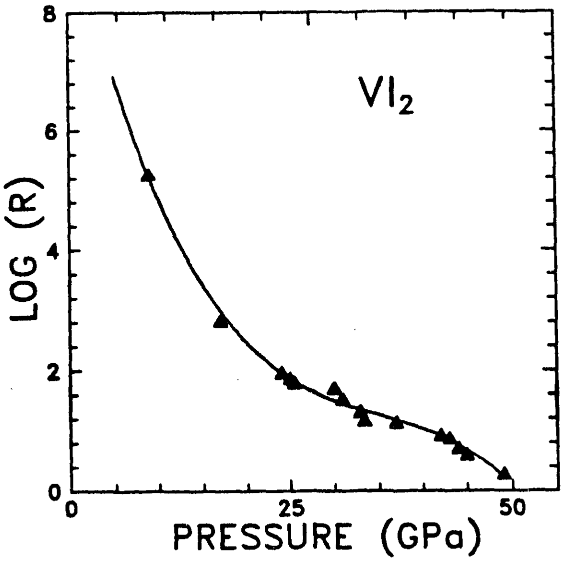

Figure 2. The pressure dependence of the Resistance of VI_2 at 300 K. The solid line is a guide to the eye. The error in pressure is ±0.4 GPa. Note the leveling off of log(*R*) near 35 GPa; an indication of possible metalization.

To measure the insulator-metal transition pressure, a series of *R*(T,P) data were recorded in the 200 - 350 K temperature range near 35 GPa. In this temperature range the *R*(T) functions displayed a linear behavior. The resistance derivative could be calculated using a least-squares-fitting program. A plot of $dR/dT(P)$ is shown in Fig. 3. There is clearly a change in sign, from negative to positive, at ~ 45 GPa. A value of P_c = 44±1 GPa is obtained from this analysis. No hysteresis was detected under decompression.

DISCUSSION

Vanadium diiodide is the lightest of the $(TM)I_2$ MI. It has the highest P_c (44 GPa) of all measured pressure-induced Mott transitions. For the *heavy* iodides, Ni, Co and Fe, values of P_c are: 19, 12 and 21 GPa respectively[5,6,7]. For Mott-Hubbard theory[8] in its simplest form it is proposed that charge fluctuations of the $d_i^n d_j^n \leftrightarrow d_i^{n-1} d_j^{n+1}$ results in an intra-band gap U. At ambient pressure it is now accepted that this mechanism is responsible for the electronic (optical) band gap in the Ti and V compounds. Zaanen et al.[9] proposed a different charge fluctuation scheme to explain the origin of the optical gap in the *heavy* TM compounds, namely, the *Charge-Transfer* mechanism. It involves the CT inter-band gap Δ and charge fluctuation of the form $d_i^n \leftrightarrow d_i^{n+1}\underline{L}$ where $\underline{L}$ denotes, in the present case, a 5*p*-hole in the iodine valence band.

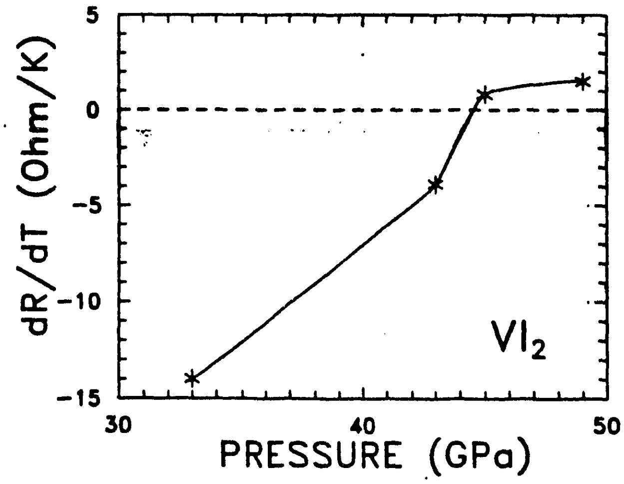

Figure 3. The pressure dependence of the resistance derivative of VI_2 at 300 K near 45 GPa. The solid line is to guide the eye. The transition from (-) to (+) values determines the pressure of the *insulator→metal* transition.

The CT mechanism, in which $E_{gap} \propto \Delta$, is explicitly proportional to the electronegativity of the anion via Δ. A pure Mott-Hubbard gap formulation does not include the ligand electronegativity, it uses a free-ion basis for the d^n configurations. Undoubtedly a better scheme would have been to incorporate *bonding and antibonding* basis functions so that much of the ground state 5*p*-3*d* hybridization is included from the outset. The exclusion of this factor in the basis functions results in intra-band gaps exceeding 5-8 eV. The relatively low experimental value of P_c for VI_2 is a clear evidence for such an extended basis function.

At this stage we assume the VI_2 gap closure to be of the Mott-Hubbard type. A better understanding of the mechanism of the gap closure will be available once the ^{129}I Mössbauer results near P_c will have been analyzed. The latter, via the Isomer Shift and magnetic interaction data will provide information[10] on the magnetic and electronic properties at and close to the Mott transition. The MS results will also permit one to check the possibility of the coexistence of the metallic and *"gapped"* states near P_c There is evidence of this coexistence in Fig. 2; namely, *R*(P) does not level off at $P \geq P_c$. A similar result was observed in CoI_2 (ref. 10) in which the metallic behavior near P_c as measured by *R*(T) was explained on the basis of a percolative system.

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