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TITLE THE PRESSURE-INDUCED MOTT TRANSITION IN TRANSITION-METAL IODIDES

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THE PRESSURE-INDUCED MOTT TRANSITION IN TRANSITION-METAL IODIDES

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Many of the Transition Metal (TM) compounds, because of exchange and correlation interactions within the narrow and poorly overlapping d-bands, become antiferromagnetic insulators, the so called Mott Insulators (MI). The properties of the MI and their gradual transition into the non-correlated metallic state (the Mott Transition) are of crucial importance for the elucidation of high temperature superconductor materials features in particular and to magnetism in general. The transition of the MI into a metal can be achieved either by selective doping or by high pressure. The first method usually fails because the electronic and structural disorder inherent in doping the narrow-band material has a strongly perturbing effect. A better way to provide definitive data on the Mott transition is to subject well characterized materials to high pressures. We have for the first time obtained extensive information on the Mott-Hubbard gap closure induced by high pressures.

Coexistence of localized moments and an insulator state is an inherent feature of the MI. Whereas the localized moments can be explained by the correlation and exchange interactions within the narrow and poorly overlapping d-bands, not a single formalism exists that predicts the insulator properties or the Mott-Hubbard gap. These insulators are predominantly antiferromagnetic, and their magnetic behavior is well explained within the framework of an effective spin Hamiltonian of the Heisenberg form. The optical gap is large (few eV), independent of temperature, and the optical absorption spectra, within the gap, exhibit the excitons predicted by crystal-field theory. Mott insulators constitute half of all binary transition metal (TM) compounds, and the majority of the TM oxides halides and chalcogenides are Mott insulators. Although the phenomenology of the MI is quite rich, information on the non-metal -metal transition, the Mott Transition (MT), is rather scarce. The MT, as such, is an event of very rare occurrence. For the case of a Mott transition, two phenomena should occur simultaneously with increasing pressure: 1 - an isostructural insulator - metal transition, and 2 - the collapse of the magnetic moment. Using the diamond anvil cell (DAC) for generating very high hydrostatic pressures, the necessary information can be obtained through electrical resistivity (R), X-ray diffraction, and Mossbauer Spectroscopy (MS) techniques. Whereas R(P,T) provide the definitive data on the transition from a gap- to a gapless-state at the critical pressure P_c the ME provides information on the state of magnetization. The X-ray diffraction is essential to confirm that the transition at P_c is isostructural and to obtain the equation of state. Such measurements on the layered compound NiI_2 have been recently reported by Pasternak et al.[1]. As was shown, the transferred hyperfine interaction at ^{129}I proved to be a very sensitive and unambiguous technique for determining P_c, surpassing the R(P,T) methods.

The dihalides of Ni and Co crystallize into structures that consist of weakly interacting slabs of I-TM-I. They order antiferromagnetically with T_N = 75 K and 12 K for NiI_2 and CoI_2, respectively. The cations are ferromagnetically ordered within each layer. Due to the crystallographic symmetry, each iodine "sits" on top of three cations belonging to a ferromagnetically ordered layer. Therefore, the transferred hyperfine interaction measured by ^{129}I MS combines a magnetic interaction whose hyperfine field H_{hf} is proportional to the Ni^{2+} moments and an electric quadrupole interaction e^2qQ whose electric-field-gradient (efg) principal axis (eq_{zz}) is along the c-axis.

Results show that the high pressure transition at P_c from a magnetic to a non magnetic state is not accompanied by a crystallographic change. Electrical resistivity studies with NiI_2 have confirmed[1] the presence of a metallic state at $P > P_c$. Another feature of the pressure behavior of the magnetic state is the gradual increase of the Néel temperature and a slight increase in the TM^{2+} moments. The collapse of the magnetic state above P_c is abrupt for some cases (NiI_2) and gradual for others (CoI_2), indicative of different band overlap mechanisms. The transition at P_c is rather sharp. The sudden delocalization of d electrons as reflected by the collapse of H_{hf} at P_C can be explained as only due to the overlap of steep bands, namely Mott-Hubbard d-d bands. The IS data in NiI_2 are consistent with such a gap closure whereas the CoI_2 closure involves the ligand 5p band as well.

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THE PRESSURE-INDUCED MOTT TRANSITION IN TRANSITION-METAL IODIDES

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ABSTRACT

Many of the Transition Metal (TM) compounds, because of exchange and correlation interactions within the narrow and poorly overlapping d-bands, become antiferromagnetic insulators, the *Mott Insulators* (MI). The properties of the MI and their gradual transition into the non-correlated metallic state (the *Mott Transition*) are of crucial importance for the elucidation of HTS materials features in particular and to magnetism in general. The transition of the MI into a metal can be achieved either by doping or by high pressure. The first method is definitely inappropriate for studying the nature of the Mott transition; for the narrow-band materials the electronic and structural disorder inherent in doping has a strongly perturbing effect. To yield the definitive data on the Mott transition high pressure work on well characterized materials should be sought. The present studies provide for the first time extensive information on the Mott-Hubbard gap closure induced by high pressure.

High pressure studies using Diamond Anvil Cells were conducted with several $(TM)I_2$ compounds. They all have layered structures and order antiferromagnetically at ambient pressure. ^{129}I Mossbauer Spectroscopy (MS) was

used to study the properties of the $(TM)^{2+}$ sublattice magnetization as a function of pressure and temperature, and X-ray diffraction was used to look for possible crystallographic transitions and to obtain the equation of state. Results show that the high pressure transition at P_c from a magnetic to a non-magnetic state is not accompanied by crystallographic changes. Previous studies[1] with NiI_2 have confirmed the presence of a metallic state at $P > P_c$. Inherent to the pressure behavior of the magnetic state is the gradual increase of T_N in all cases and a slight increase in the TM^{2+} moments with pressure increase. The collapse of the magnetic state is abrupt for some cases (NiI_2) and gradual for others (CoI_2), indicative of different band-overlap mechanisms.

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INTRODUCTION

Coexistence of localized moments and an insulator state is an inherent feature of the so called *Mott Insulators*[1] (MI). Whereas the localized moments can be explained by the correlation and exchange interactions within the narrow and poorly overlapping *d*-bands, not a single formalism exists that predicts the insulator properties or the Mott-Hubbard gap[2]. These insulators are predominantly antiferromagnetic, and their magnetic behavior is well explained within the framework of an effective spin Hamiltonian of the Heisenberg form. The optical gap is large (few eV), independent of temperature, and the optical absorption spectra, within the gap, exhibit the excitons predicted by crystal-field theory. Mott insulators constitute half of all binary transition-metal (TM) compounds. and the majority of the TM- oxides, -halides and -chalcogenides are Mott insulators. Although the phenomenology of the MI is quite rich[3], information on the non-metal - metal transition, the *Mott transition*[4] (MT), is rather scarce. The MT, as such, is an event of very rare occurrence. The recent discovery of the ternary and quaternary cuprates high temperature superconductors materials has significantly enhanced the interest in the properties and nature of the Mott transition.

The onset of a Mott transition is achieved either by alloying (doping) or by pressure. Unlike classical semiconductors, doping of narrow-band materials introduces severe electronic and structural disorder. Disorder simply enhances the intertwining of Mott localization with Anderson disorder-induced localization[5,6]; therefore, closure of the Mott- Hubbard gap by hydrostatic pressure will be the "cleanest" way to investigate this intricate insulator- metal transition.

For the case of a Mott transition, two phenomena should occur simultaneously with increasing pressure: 1 - an isostructural insulator - metal transition, and 2 - the collapse of the magnetic moment. Using modern techniques for generating very high hydrostatic pressures, the necessary information can be obtained with Diamond Anvil Cells (DAC) in conjunction with *resistivity* (R), *x-ray diffraction, and Mössbauer Spectroscopy* (MS) methods. Whereas R(P,T) provide the definitive data on the transition from a gap- to a gapless-state at the critical pressure P_c, the ME provides information on the state of magnetization. The x-ray diffraction is essential to confirm that the transition at P_c is isostructural. Such measurements on the layered compound NiI_2 have been recently reported by Pasternak et al.[6]. As was shown, the transferred hyperfine interaction at ^{129}I proved to be a very sensitive and unambiguous technique for determining P_c, surpassing the R(P,T) methods. In the present paper we review the NiI_2 results and present new MS results on CoI_2, an analogous, layered Mott insulator.

The dihalides of Ni and Co crystallize in the $CdCl_2$ and $Cd(OH)_2$ structures, respectively[7]. These structures consist of weakly interacting slabs of *I-TM-I.* In the hexagonal lattice each unit cell contains three formula units stacked in a staggered fashion along the c axis. They order antiferromagnetically with T_N = 75 K and 12 K (ref. 8) for NiI_2 and CoI_2, respectively. The cations are ferromagnetically ordered within each layer[9]. Due to the crystallographic symmetry, each iodine "sits" on top of three cations belonging to a ferromagnetically ordered layer. Therefore, the transferred hyperfine interaction measured by ^{129}I MS combines a magnetic interaction whose hyperfine field H_{hf} is proportional to the Ni^{2+} moments and an electric quadrupole interaction e^2qQ whose electric-field-gradient (*efg*) principal axis (eq_{zz}) is along the *c*-axis.

EXPERIMENTAL

Sample Preparation and the High Pressure Method. Both iodides were prepared by solid-gas reaction of stoichiometric amounts of the appropriate elements at elevated temperatures in evacuated quartz ampoules. For the MS samples, molecular I_2 enriched with ^{129}I was obtained from specially prepared PdI_2 by thermal decomposition. For the other measurements, samples were prepared from high-purity, naturally abundant elements. Samples were loaded into the DAC under an inert-gas atmosphere. For MS studies a modified Merrill-Bassett DAC was used with a TaW alloy gasket that also served as a γ-ray collimator[10]. Piston-cylinder-type cells were employed for the electrical and x-ray studies. Argon was used as the pressurizing medium in the MS studies, $CaSO_4$ in the resistance measurements[10, 11], and nothing in the x-ray measurements. A quasi-four point method was employed for the electrical resistance measurements. Pressures were measured *in situ* by the ruby fluorescence technique[12].

The Mossbauer Effect Measurements. Absorbers were typically 0.25-mm diameter and 2-3 mg/cm^2 thickness in ^{129}I. The single line 27.8-keV γ-ray

^{129m}Te sources were prepared by a month-long thermal-neutron irradiation of Mg_3TeO_6 ceramic disks made using ^{128}Te enriched oxides. At selected pressures, the temperature dependence of the relative magnetization (*via* H_{hf}), the Neel temperature, and the isomer shift were determined.

RESULTS

Mössbauer Spectroscopy. ^{129}I MS measurements were obtained for NiI_2 and CoI_2 at pressures up to 28 GPa and temperatures from 4 to 315 K. At $T > T_N$ the spectra were fitted assuming an axial-symmetric *efg*. For NiI_2 and CoI_2 values of e^2qQ at ambient pressure were 5.4(2) and 4.6(2) mm/sec, respectively. At $T < T_N$ spectra were fitted assuming a combined magnetic-quadrupolar interaction. The following spin-Hamiltonian *H*, (adequate for the case where $\mu H_{hf}/I \gg e^2qQ/4I(2I-1)$), acting on the excited ($I^*=5/2$) and ground ($I=7/2$) states was applied:

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

where θ is the angle between eq_{zz} and H_{hf}. Note that for the special case of $\theta \approx 55^\circ$ the quadrupolar term in (1) vanishes so that a "symmetric" Mössbauer absorption spectrum will result. Thus the value of e^2qQ is determined from measurements at $T > T_N$, and this spectral feature allows the determination of θ. For NiI_2 it has been previously determined[13,14] that θ is close to 55°. For CoI_2 it has been suggested by Kuindersma et al.[9] that $\theta = 90^\circ$, which would produce a non-symmetric spectrum. But as can be seen from Fig.3, this is not the case. We have concluded that for CoI_2 $\theta = 55^\circ(5)$[15]. In both iodides no variation in θ with pressure has been detected.

Nickel iodide. The pressure dependence of $Ni^{129}I_2$ MS parameters are depicted in Fig. 2. The upper part (c) shows the pressure dependence of T_N[16]. Fig 2(b) depicts the pressure dependence of H_{hf} at saturation (H_{hf}^{sat}) measured at $T \ll T_N$. The pressure at which H_{hf}^{sat} vanishes was defined as the "critical pressure" P_c. As will be shown, P_c coincides with the transition from the correlated, gap-state to the uncorrelated, metallic sate. The pressure dependence of the Isomer Shift (IS) is depicted in Fig. 2a. Characteristic to NiI_2 results are: 1 - monotonic increase of IS(P), namely, a smooth increase in the *s*-electron density at the nucleus with no discontinuity at P_c, 2 - $H_{hf}(P)$ remains constant up to $P \cong 13$ GPa after which it slightly decreases, and dramatically vanishes at $P \simeq 19$ GPa (P_c), and 3 - a substantial enhancement of T_N with increasing pressure.

Cobalt iodide. Similar procedures were applied to analyze the $Co^{129}I_2$ MS data. In Fig. 3 we depict typical spectra measured at 4 K covering the pressure range of 0 - 13 GPa. In contrast to NiI_2, close to P_c (~ 12.5 GPa), two spectral sites are observed. In the pressure range of 9 - 13 GPa, the fitting were carried out by deconvoluting into two subspectra corresponding to a magnetic and a non-magnetic site. At $P \geq 13$ GPa, only the non-magnetic site is measured. This is summarized in Fig. 4: H_{hf}^{sat} *increases* with P and in the range of 9 GPa to P_c, the magnetic (square symbols) and the non-magnetic (circles) regimes coexist (Fig. 4b). The relative abundance of the two regimes is plotted in the insert. In Fig. 4a we depict the IS(P). As can be seen, the non-magnetic and the magnetic states are characterized by different IS. As in NiI_2, T_N increases with P, however in CoI_2 the increase is dramatic (Fig. 4c); from T_N = 12 K at ambient pressure to 125 K close to P_c the increase is 10- fold whereas in NiI_2 the increase in is "merely" 4-fold.

X-ray diffraction and Conductivity. The reduced volume of NiI_2 as a function of pressure is shown in Fig. 5. No crystallographic phase transition is observed at P_c. The solid line is a least-squares fit to Birch-Murnaghan equation of state yielding a value $K_0 = 27.7(1)$ GPa for the bulk-modulus and a value $K'_0 = 4.8(2)$ for its pressure derivative. Conductivity measurements carried out by a quasi-four point method[11] produced the following observations[6]: 1 - An "infinite" resistance at $P < 5$ GPa, 2 - A linear decrease in *log*(R) with increasing pressure in the pressure range 5 - 16 GPa, 3 - A slope increase in the 16 - 18 GPa range, and 4 - Leveling off at $P \geq 18$ GPa. Measurements of R *versus* temperature in the vicinity of P_c clearly suggests a metallic state at $P > P_c$ in contrast to the semiconducting behavior at $P < P_c$. No x-ray or conductivity data are as yet available for CoI_2. It is therefore assumed, as was the case for NiI_2, that the $P_c(CoI_2)$ determined by MS signals the isostructural, gap- to a gapless- state transition.

DISCUSSION

A common feature of the structurally analogous Ni and Co iodides is the drastic increase of the Néel temperature with decreasing volume. This reflects the increase of the wave-function overlap which affects the various exchanges (direct, indirect and superexchange). The difference between the increase of T_N with P in CoI_2 and NiI_2 could be due the fact that the orbital term of the Co^{2+} (d^7) moment is not completely quenched as is the case for Ni^{2+} (d^8). Another consequence of the possible unquenched *g*(orbit) will be a band anisotropy in the *k*-space, which would account for the coexistence of the two regimes near P_c. This coexistence *is not observed* in NiI_2, whose *g*-value is isotropic. According to the Hubbard-Mott model, the moment should monotonically decrease with increasing pressure, vanishing at P_c. The fact that $H_{hf}^{sat}(CoI_2)$ *increases* with pressure and suddenly vanishes at P_c can only be explained as due the contribution of g(orbit).

The nature of the Mott insulators, including the failure of conventional band structure to explain the existence of the band gap, has been extensively discussed[1]. Numerous experiments in MI compounds carried out by x-ray, optical, and photoemission spectroscopies provided important information on the excitations within the gap[17]. According to the Mott-Hubbard theory[2], charge fluctuations of the type $d_i^n d_j^n \leftrightarrow d_i^{n-1} d_j^{n+1}$, which involves the *d-d* Coulomb and exchange interactions (U), solely determines the nature of the band gap. However, a model proposed by Zaanen, Sawatzky, and Allen[18] (ZSA) invokes the participation of another charge fluctuation energy Δ through the Charge Transfer (CT) mechanism,

$$d_i^n \rightarrow d_i^{n+1}\underline{L} \tag{2}$$

where $\underline{L}$ denotes a hole in the anion valence band. According to ZSA's model, for the heavier TM compounds ($U > \Delta$) the transitions within the gap will be of the CT type, whereas for light TM compounds ($U < \Delta$) the *d-d* type dominates. In the present case we expect the first type to be dominating. And in fact, photoemission experiments in NiI_2,[17,19] invoke the CT type fluctuation, involving the $5p^6 3d^8 \leftrightarrow 5p^5 3d^9$ transition. The question arises whether with increasing pressure and at the "gap closure" (at P_c) the CT mechanism still dominates. As a consequence of the gap closure, a *p*-hole in the iodine 5*p* band will be created . The IS, due to its sensitivity to the *p*-holes in the $5p^6$ valence band, plays a unique role in unraveling the gap-closure mechanism.

From electron density calculations it was realized[20] that the IS of 5*sp* elements can be approximated by a linear dependence on the number of *s* holes (h_s) and *p* holes (h_p) in the full $5s^2p^6$ shell. For the present case we neglect transitions through the 5*s* band. According to Van der Heyden et al.[21], the expression for IS(h_p) with respect to Mg_3TeO_6 is:

$$IS = 1.27h_p + 3.58 \text{ mm/sec.} \tag{3}$$

Using the value of 3.80(5) mm/sec for the IS(CoI_2) obtained at ambient pressure we deduce a value of h_p = 0.17, which arises due to covalency. The same value, within the experimental error, was found for NiI_2. Thus, at ambient pressure the I^{-1} configuration is $5s^2p^{5.83}$. At P_c we observe a discontinuous increase in IS by 0.20(4) mm/sec (see Fig. 4a) which according to Eq. 3 corresponds to the creation of 0.16 *p*-holes or according to Eq. 2 to $\underline{L}$ = 0.15 *per* iodine. Thus, the onset of a metallic, uncorrelated state is accompanied by a transfer of 0.32e^- from the iodine valence 5*p*-band into the cobalt conduction 3*d*-band. This of course does not preclude a *d*-*d* intra-band closure as well.

CONCLUSION

The combined methods of MS, x-ray diffraction, and conductivity proved to be essential to establish the existence and nature of the pressure-induced Mott transition in the layered compounds NiI_2 and CoI_2. It was demonstrated that the collapse of the moment concomitant with isostructural insulator-metal transition are inherent phenomena associated with the MT. The transferred hyperfine interaction was shown to be a very sensitive probe for determining P_c. Though structurally analogous, the pressure dependence of the moments and T_N and the gap closure of the two iodides are quite different. It is concluded that the orbital contribution of the moment in CoI_2 may play an essential role in determining the various exchange interactions and the coexistence of the correlated and uncorrelated states in the vicinity of P_c.

The transition at P_c is rather sharp. The sudden delocalization of *d*-electrons as reflected by the collapse of H_{hf} at P_c can be explained as only due to the overlap of steep bands, namely Mott-Hubbard *d*-*d* bands. The IS data in NiI_2 are consistent with such a gap closure whereas the CoI_2 closure involves the ligand 5*p* band as well. Further experiments with other $(TM)I_2$ are now in progress. We believe such experiments will further elucidate this exciting and fundamental branch of the more general area of metal-insulator transitions.

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Figure Captions

Fig. 1 - $Ni^{129}I_2$ Mössbauer spectra at 6.7 GPa and various temperatures. The solid line is a theoretical spectrum obtained from the least-squares fit of the spin-Hamiltonian.

Fig. 2 - The pressure dependence of the relevant MS parameters in NiI_2. *a* - The isomer shift. Note the monotonic increase with P. No discontinuity is observed at P_c. *b* - The hyperfine field. H_{hf}^{sat} remains constant to P ≈ 13 GPa, decreases slightly near 18 GPa,then vanishes at P ≅ 19 GPa (P_c). *c* - The Néel temperature. Solid lines are an aid to the eye only.

Fig. 3 - The Mössbauer spectra of $Co^{129}I_2$ at T ≤ 4 K as a function of pressure. Note the coexistence of two sites at P = 9.5 and 11.8 GPa, corresponding to magnetic/quadrupolar and quadrupolar interactions. The fit was carried out assuming such interactions with free relative intensities (abundances). At 13 GPa only a quadrupole splitting is present.

Fig. 4 - The pressure dependence of the relevant MS parameters in CoI_2. The (□) corresponds to the magnetic and the (○) to the non-magnetic species. *a* - The isomer shift. Note the difference in IS between the non-magnetic and the magnetic states. *b* - The saturation hyperfine field. Note the increase in $H_{hf}^{sat}(P)$ up to $P = P_c$ = 12.5 GPa. H_{hf}^{sat} = 0 for the non-magnetic, presumably metallic state. The insert shows the variation of the relative abundance of the two sites in the coexistence region. *c* - The Néel temperature. Solid lines serve only to guide the eye.

Fig. 5 - The normalized volume of NiI_2 *versus* pressure at 300 K as measured by angle-dispersive X-ray diffraction. The solid curve is a least-squares fit to the Birch-Murnaghan equation (see text). The uncertainties in V/V_0 are ± 0.003. No significant change is found at P_c in V/V_0 or its derivative.

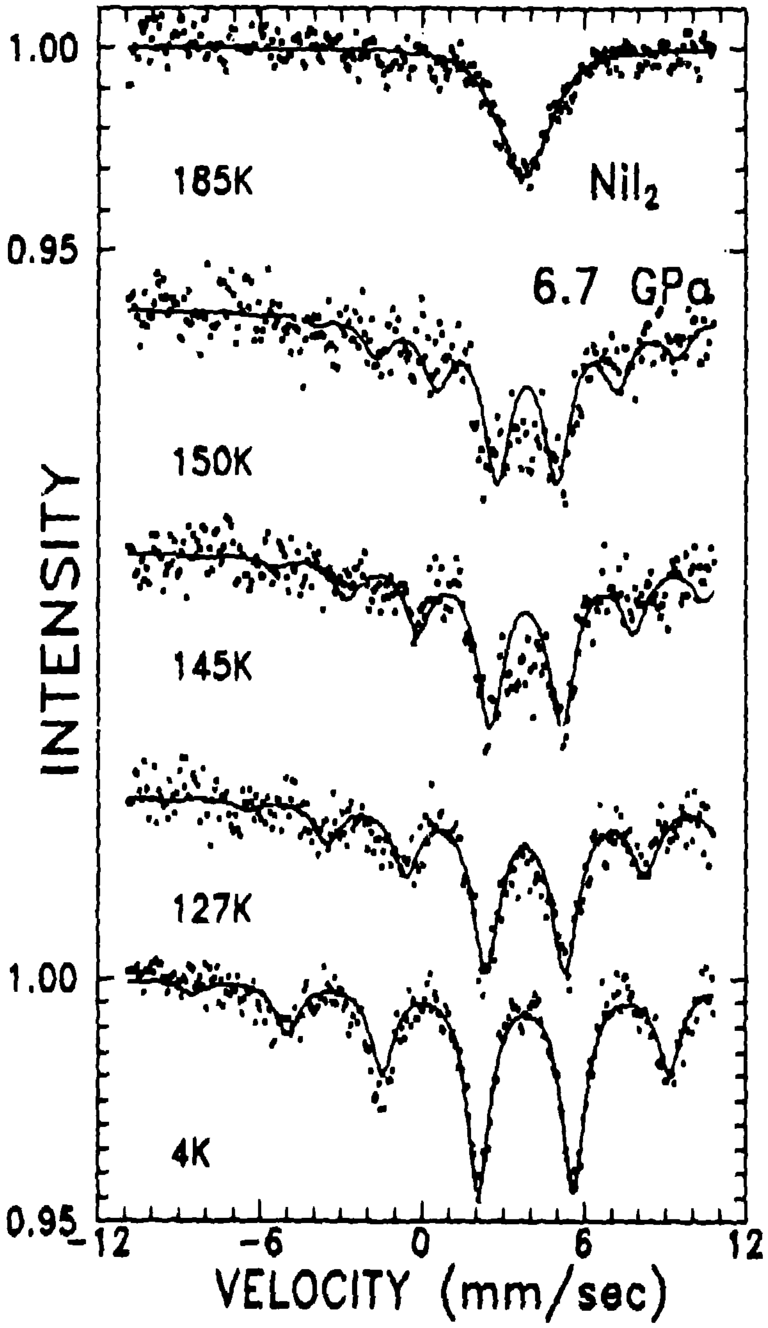

fig.1 Pasternak, Taylor, Jeanloz

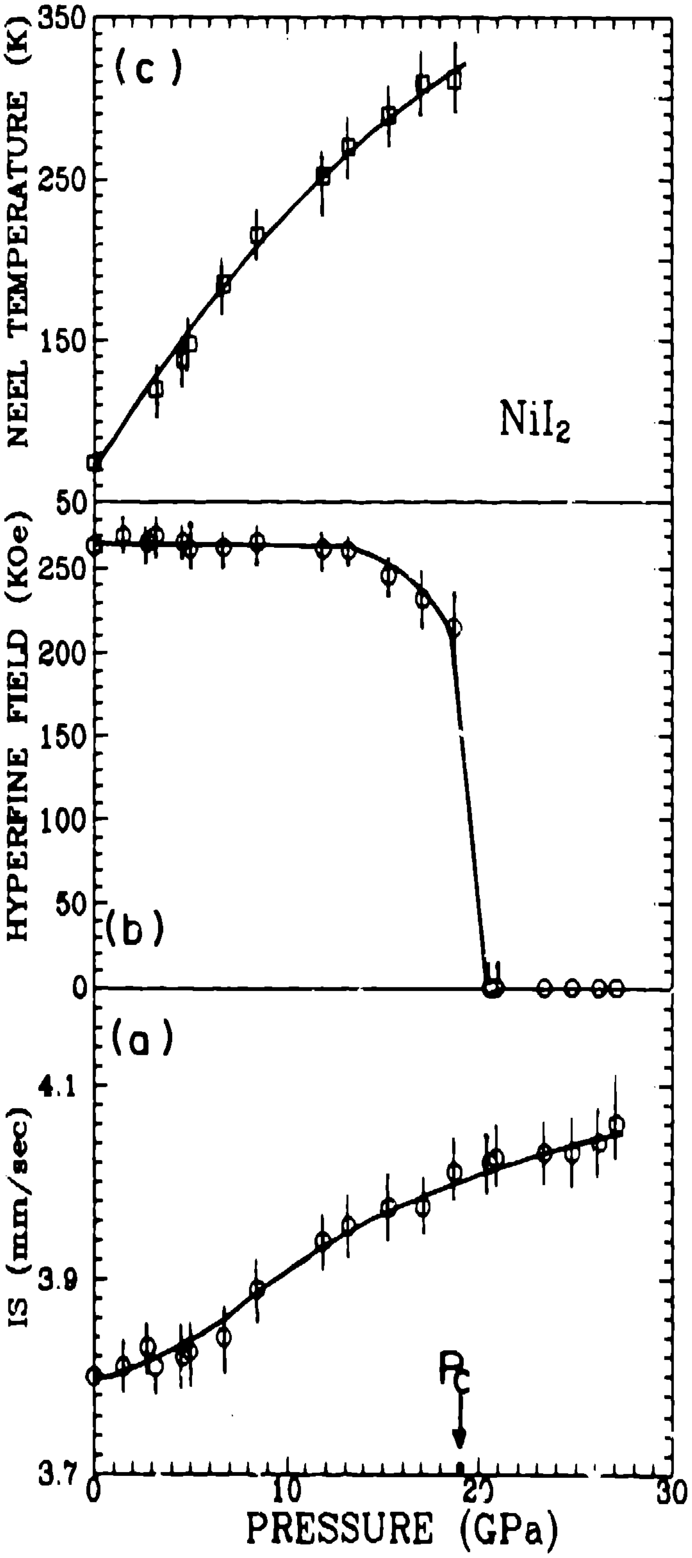

Fig 2 Pasternak, Taylor, Jeanloz

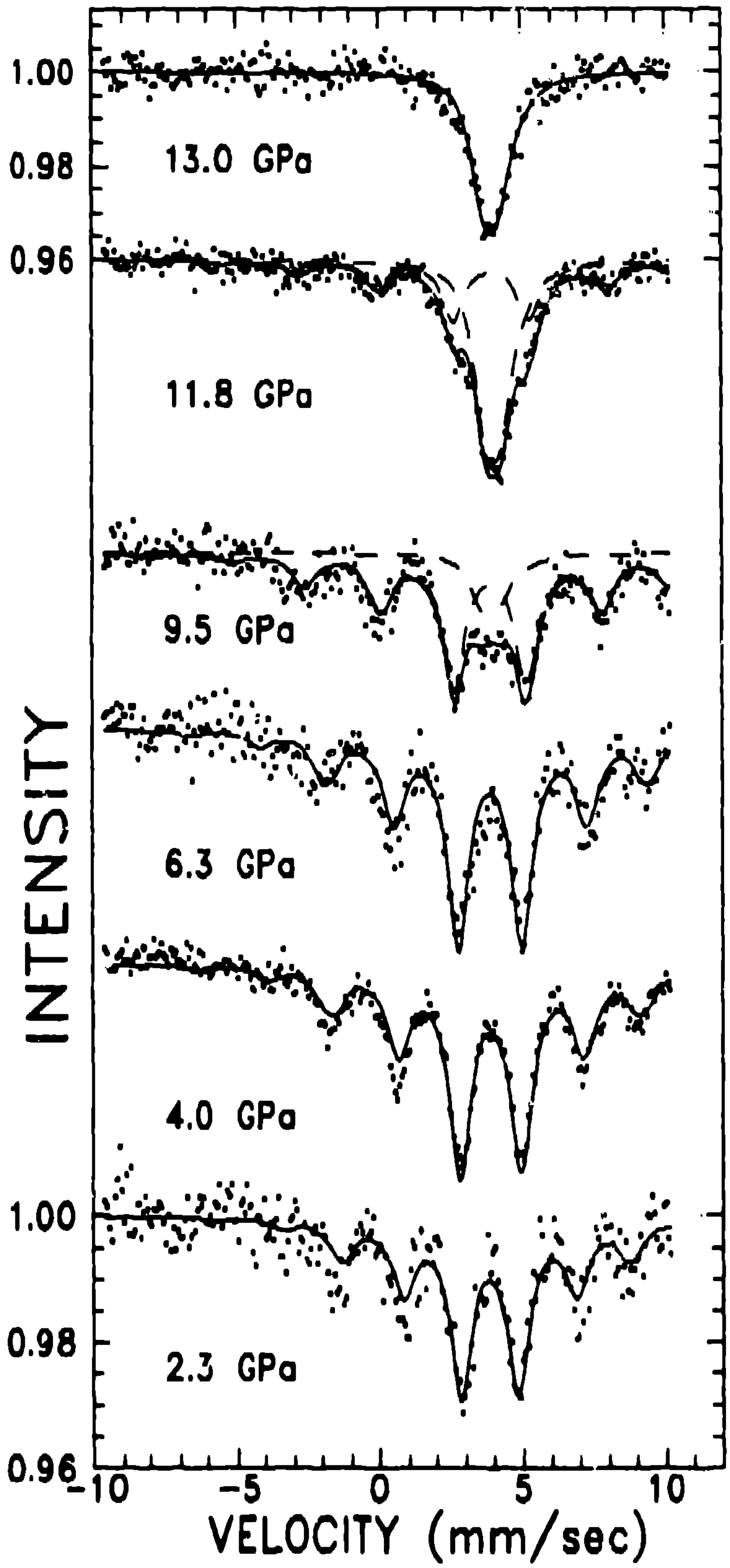

Fig 3 Pasternak, Taylor, Jeanloz

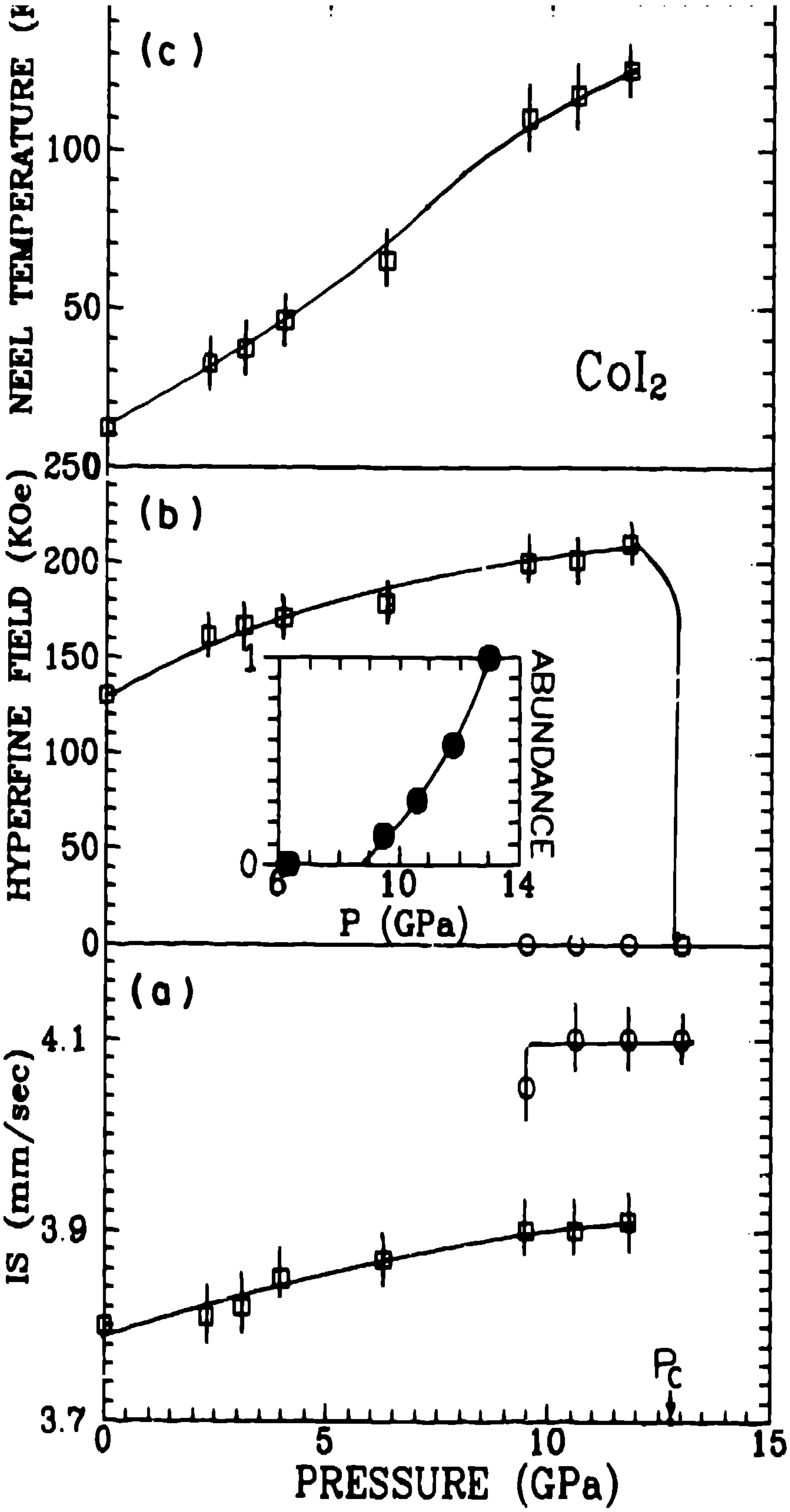

Fig. 4 Pasternak Taylor Jeanloz

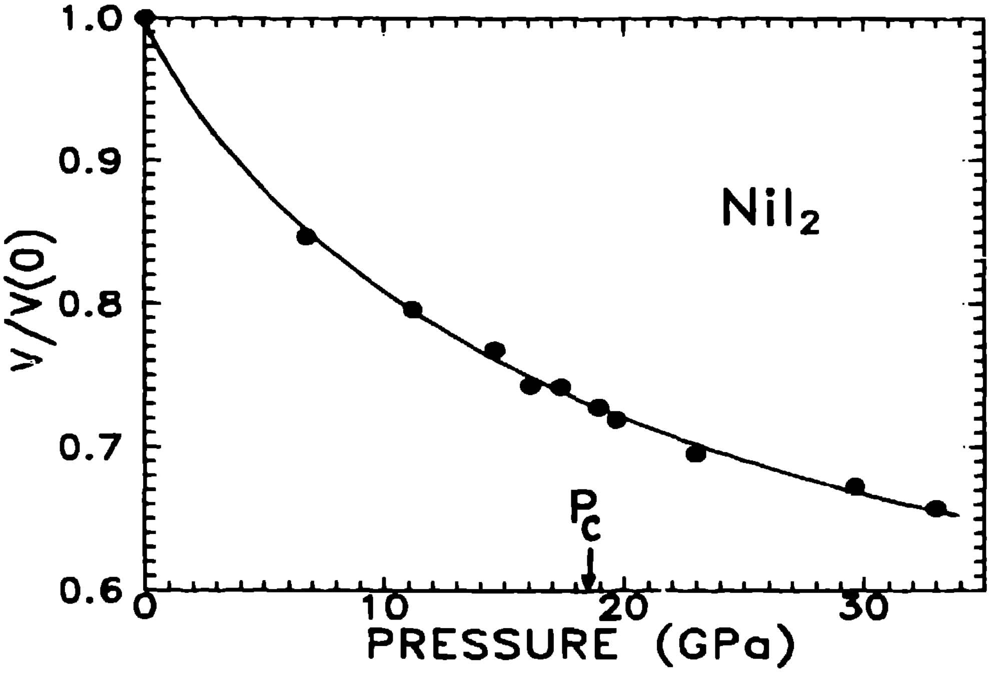

Fig 5 Pasternak Taylor Jeanloz