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AUTHOR(S) R. D. Taylor, M. P. Pasternak

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HIGH PRESSURE MÖSSBAUER SPECTROSCOPY IN DIAMOND ANVIL CELLS

R. D. TAYLOR
Physics Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

and

M. P. PASTERNAK
School of Physics and Astronomy, Tel Aviv University, Ramat Aviv 69978, Israel, and Physics Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

Diamond anvil cells provide a means to obtain near-hydrostatic pressures from the kilobar to the megabar regime. Mössbauer spectroscopy (MS) nicely complements the optical and X ray measurements usually made. After a brief summary of the techniques applicable to MS, we present several examples of high pressure MS including hysteresis in the α-ε transition in Fe, metallization in molecular crystals and the insulator-metal Mott transition in NiI_2 and CoI_2.

1. Introduction

Static high pressures have been used to augment Mössbauer Spectroscopy (MS) since the early sixties. Pressures to about 20 GPa were available using modified Bridgman anvil presses [1]. The "pressure clamp" technique was soon adapted to to provide a compact device for pressures up to about 10 GPa that could be readily loaded with rather large MS samples and be cooled to cryogenic temperatures [2]. The first MS carried out in a diamond anvil cell (DAC) was reported [3] in 1965 for $^{119}SnO_2$; the first ^{57}Fe-containing absorber work was reported [4] in 1975; and the first source experiments were reported [5] in 1982. The ease of measuring pressure and pressure gradients *in situ* via the pressure shift of the laser-excited ruby fluorescence has contributed to the quickened pace since then. The highest pressure MS reported to date was for Fe_2O_3 at 72 GPa [6] (720 kbar). Reviews of techniques and applications of DAC's [7] and of DAC-MS [8-10] are available. MS nicely complements the X-ray, optical and resistivity techniques usable in DAC's and provides a versatile microscopic probe through the sensitivity of the hyperfine parameters to high pressures. In this paper we will highlight some of the DAC features and illustrate DAC-MS with a few examples.

2. Techniques

High pressures are obtained simply by applying modest axial forces to the faces of two opposing modified brilliant-cut diamonds whose small culet tips have been ground flat. Pressures as high as 416 Gpa [11] have been generated using <50-micron beveled tips. Usually a thin gasket material is placed between the culet tips to help support the load; a hole drilled in the prepressed gasket defines the sample space. The space (typically 150- to 300-microns diameter by 10- to 50-microns thick for MS) contains the sample, ruby chips for determining the pressure and a pressurizing medium for reducing pressure gradients. For MS a high *Z* gasket material is selected to serve as a γ-ray collimator. This configuration is shown schematically in fig.1. High quality, modified gem stones of 0.1- to 0.4-caret weight are commercially available.

The cells designed to align the opposed diamond pair and to provide the closure thrust take on a variety of forms [7], but most are modifications of either the Merrill-Bassett triangular thrust plate type or the Mao-Bell rocking anvil piston-cylinder type [8-10]. A cross section of the former is shown in fig. 2 in a configuration used in MS. The cell consists of the following : 1) two triangular platens with alignment pins and three screws used to supply the closure force on the centrally located diamonds; 2) two backing plates with conical apertures for epoxy-mounting the diamonds. One is rigidly located in its platen, the other is adjustable laterally using three fine screws (not shown) to locate the diamonds on the same axis; 3) diamond anvils chosen to meet the needs of sample size, pressure range, thickness and cost; and 4) gasket selected to provide diamond support, sample collimation and ease of preparation. After the diamonds are aligned to be parallel and on axis, the gasket is emplaced, prepressed to desired sample thickness and drilled. The sample and ruby chips are loaded, and the sample space is sealed off with a pressurizing medium such as liquid argon [9]. The pressure is raised by tightening the three screws so as to maintain the parallel alignment. The diamond windows provide easy visual access to observe the sample and to laser-excite and measure the ruby fluorescence. Such cells have been used for MS up to 40 GPa.

The piston-cylinder pressure cell provides a more precise closure mechanism and hence is capable of much higher ultimate static pressures [7-11]. A sketch of such a cell adapted for MS is shown in fig. 3. The diamonds are located on-axis in a closed-end cylinder and a tight-fitting piston to allow precise non-shearing closure. The anvils are mounted on crossed hemi-cylinders located on the end of the piston and in the inner end of the cylinder to allow both axial and parallel alignment. An optical axis is provided through the members. A variety of mechanisms have been devised for supplying the closure thrust. Piston-cylinder cells are deemed more difficult to use for MS and are more costly to build and operate than the simpler Merrill-Bassett-type cell.

The most restrictive consideration of MS in DAC's is the extremely small sample size, typically 10^{-5}-10^{-4} g. On the other hand MS requires no leads or other communication with the sample. The richness of MS as a microscopic probe is through the pressure effects on the structure, isomer shift, recoil-free fraction and hyperfine fields of a number of isotopes in a variety of hosts. MS usually provides truly unique information. Attenuation of the MS γ rays by the anvils, especially those above 20 keV, is acceptable. Collimation of the γ rays by the Ta-W gaskets is adequate at least for energies up to 35 keV. Transmission and scattering of accompanying high energy γ rays and X rays from the source passing through the cell can increase the background count in the Mössbauer γ-ray window, but using "point sources" located very close to the cell, optimizing the detector and its geometry, and external collimation can provide significant improvements. A typical MS datum in a DAC requires accumulation times from a half day to a few days.

New cell designs for MS have emphasized miniaturization to assist in combining DAC's with cryostats, dilution refrigerators [5], superconducting magnets [12], and furnaces. A compact Merrill-Bassett-type cell [13] only 2.2-cm diam. will fit in a simple 10-T solenoid and provide pressures to >40 GPa. It is available commercially made from *Inconel* or beryllium-copper [14].

3. Selected examples of DAC-MS

3.1. EPSILON IRON

^{57}Fe MS in DAC's is hampered by the attenuation of the 14.4-keV γ ray by the diamonds. Nevertheless, both source [5,12] and absorber [6,15] data on the bcc to hcp (α-Fe to ε-Fe) phase transition in Fe have been reported. The nonmagnetic nature of ε-Fe is well established from MS measurements of the magnetization at pressure. There is a great deal of interest amongst geophysicists concerning pressure hysteresis in earth mantle-core systems [16]. The α- to ε-Fe transformation is quite sluggish with an onset reported from 8.6 to 15 GPa and a transition width from 1 to 15 GPa [15]. The transformation can be followed quantitatively by MS from the magnetic hyperfine split presence of α-Fe and the unsplit presence of ε-Fe. Similarly the ε/α abundances can be determined for decreasing pressures. In fig. 4 we present the abundance $\varepsilon/(\alpha+\varepsilon)$ for Fe as a function of increasing and decreasing pressure. The Fe absorber/argon medium results (⊕, ⊙, —) are slightly displaced from the ^{57}Co(Fe) source/alcohols results (+). Note the sluggish transition and the hysteresis width. In the inset below the graph are the onset-completion ranges for the α to ε transition compiled [17] for various pressurizing media using mostly X-ray data. The sensitivity of MS to minute levels of ε-Fe show the range to be wider than given [17] for the same medium. The top inset shows the ranges for the ε to α transition with decreasing pressure for various media. Again the range is somewhat larger for the MS results. It has been suggested [17] that the onset and range are dependent upon the shear strength of the pressurizing medium. Interestingly, the width of the hysteresis, taken as the difference in the transition midpoints for a given medium are almost constant (6.2 ± 0.2 GPa) in agreement with the MS results.

3.2. MOLECULAR CRYSTALS

The search for metallic hydrogen has spurred interest in the mechanisms of pressure-induced metallization of molecular crystals. An important issue has been the molecular *dissociation* under pressure as a prerequisite for metallization. We have studied a number of molecular crystals that become become metallic under pressure using both ^{119}Sn and ^{129}I MS. Studies of diatomic I_2 [18] and tetrahedral SnI_4 [19] and GeI_4 [20] molecular crystals to pressures of 35 GPa have revealed interesting features concerning structural evolutions under pressure, leading to metallization. In I_2, the approach to metallization occurs in two steps: 1) molecular association starting at P = 17 GPA, forming a quasi-one dimensional conducting zigzag chain and 2) chains overlap at P > 21 GPa in the *ab* plane. This interchain association is reflected in the metallic properties leading to superconductivity at T < 1.5 K [21] and is considered to be the precursor to the molecular dissociation that eventually takes place.

In the tetrahedral molecular crystals the onset of metallization is coupled with molecular association involving two of the iodines of each of the tetrahedra; the HP1 phase. The molecular association results in a crystallographic disorder as observed by X-ray diffraction. This transformation is gradual with pressure increase where the molecular and the HP1 phases coexist. We observe that there is an impressive pressure hysteresis. The ^{119}Sn MS reveals a gradual transformation of the Sn^{4+} ground state from a 5s5p to a hybridized 5s5p4d configuration and strong evidence for the persistence of a symmetric tetrahedral structure. In GeI_4 HP1 and another structural phase (HP2) were identified, the latter involving all four iodines. Recent high pressure conductivity studies [22] confirm our proposed model of structural coexistence in the hysteresis pressure zone. Proposed schematics of HP1 and HP2 are shown in figs. 5 and 6, respectively. Without question, the ^{129}I MS spectral features such as the electric-field-gradient, the assymmetry parameters, isomer shift and relative spectral abundances proved to be an unique tool for characterizing structures on a molecular scale.

3.3. MOTT TRANSITION IN NiI_2 AND CoI_2

NiI_2 and CoI_2 are layered compounds that are antiferromagnetic insulators, so-called Mott insulators [23]. Mott insulators may undergo a transition into a metallic state, the Mott Transition (MT), brought about by altering the band structure through alloying or by pressure. High pressure MS of ^{129}I provides a unique tool for studying these important systems. In particular MS, through the transferred magnetic interaction, allows determination of the magnetization and T_N with pressure. It is expected that the isostructural insulator-metal transition is accompanied by the collapse of the magnetic moment.

We have combined MS-DAC studies with X-ray structure and electrical resistivity data to characterize the MT in NiI_2 [24]. ^{129}I spectra for NiI_2 taken at 6.7 GPa and a number of temperatures are shown in fig. 7; the collapse of the magnetic interaction provides a determination of T_N, which rises linearly with decreased volume from 75 K at ambient pressure to 310 K at 19 GPa. The saturation hyperfine field (a measure of the magnetic moment) is almost constant for $P < 17$ GPa. Above a critical pressure $P_C = 19$ GPa the magnetism in NiI_2 disappears, the saturation hyperfine field goes to zero. The isomer shift varies linearly with volume up to at least 26 GPa. The data are interpreted [24] as confirmation of a pure insulator-metal transition accompanied by an antiferromagnetic-diamagnetic transition, the MT.

Data for CoI_2 are similar [25] with T_N going from 12 K at $P = 0$ to 125 K near $P_C \approx 12.5$ GPa. Just below P_C there is a small region of coexistence of magnetic and nonmagnetic sites. There are other differences in detail from the NiI_2, but CoI_2 is another good example of the MT.

4. Conclusions

It has been demonstrated that MS can be used successfully in conjunction with DAC's with very few restrictions. DAC-MS often provides truly unique information concerning magnetization, phase transformations, multiple sites, coexistence, bonding, isomer shifts, valence, and local symmetry. Most Mössbauer isotopes with energies above 14 keV can be employed in DAC's either as absorbers or as sources.

Acknowledgments

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Figure Captions

Fig.1. The heart of the diamond anvil cell: (1) Diamond anvils, (2) anvil table, (3) parallel flattened culet tip, (4) precompressed metallic gasket, and (5) drilled sample space for sample, ruby chips and pressurizing medium.

Fig.2. MS layout using Merrill-Bassett DAC. Cross section of the triangular-shaped cell: (1) High-strength platens with three thrust screws, (2) hardened backing disks for mounting and locating the diamonds, (3) metal gasket to support the anvils, provide sample space and collimate γ rays, (4) diamond anvils (with detail), (5) close coupled Mössbauer source, (6) gasket detail showing diamond support and drilled sample space (7) ruby chips for determining pressure in DAC and (8) absorber and pressurizing medium.

Fig.3. Sketch of a Mao-Bell-type cell modified for MS. The diamonds are glued to the crossed tungsten carbide rockers (1,2), which allow translational and rotational pre-alignment before prepressing a gasket. Other components are: (3,4) close fitting cylinder-piston, (5) thrust ring, (6) six closure screws and (7) Mössbauer source.

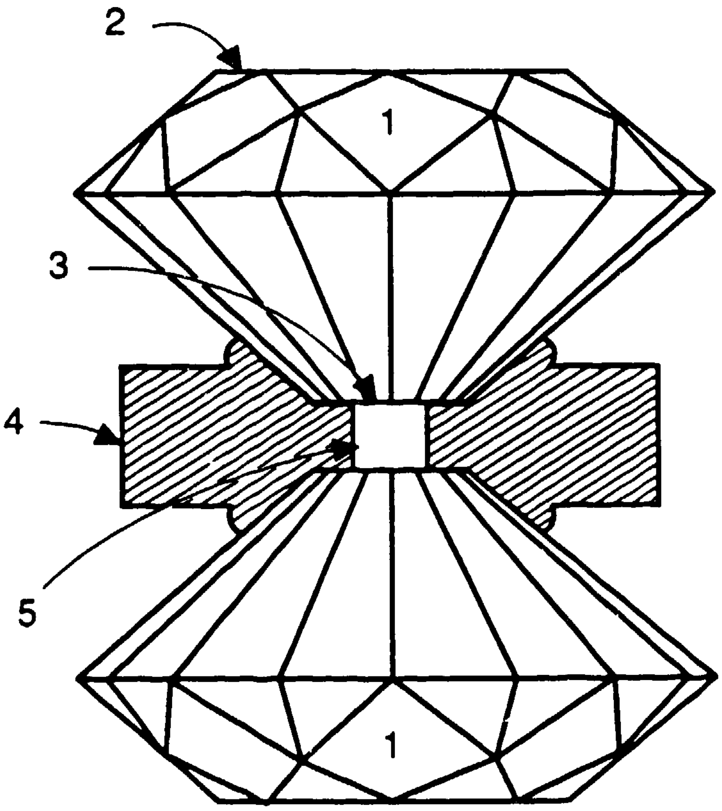
Fig.4. Relative abundance of ε-Fe resulting from rt pressurization of α-Fe and subsequent abundance upon depressurization. ^{57}Fe data for a pressurized source (+) and absorber(⊕,⊙) demonstrate a large hysteresis. Below the graph are the "onset-completion" results [17] reported for the $\alpha \longrightarrow \varepsilon$ transformation using other techniques and pressurizing media. The inverse process is shown above.

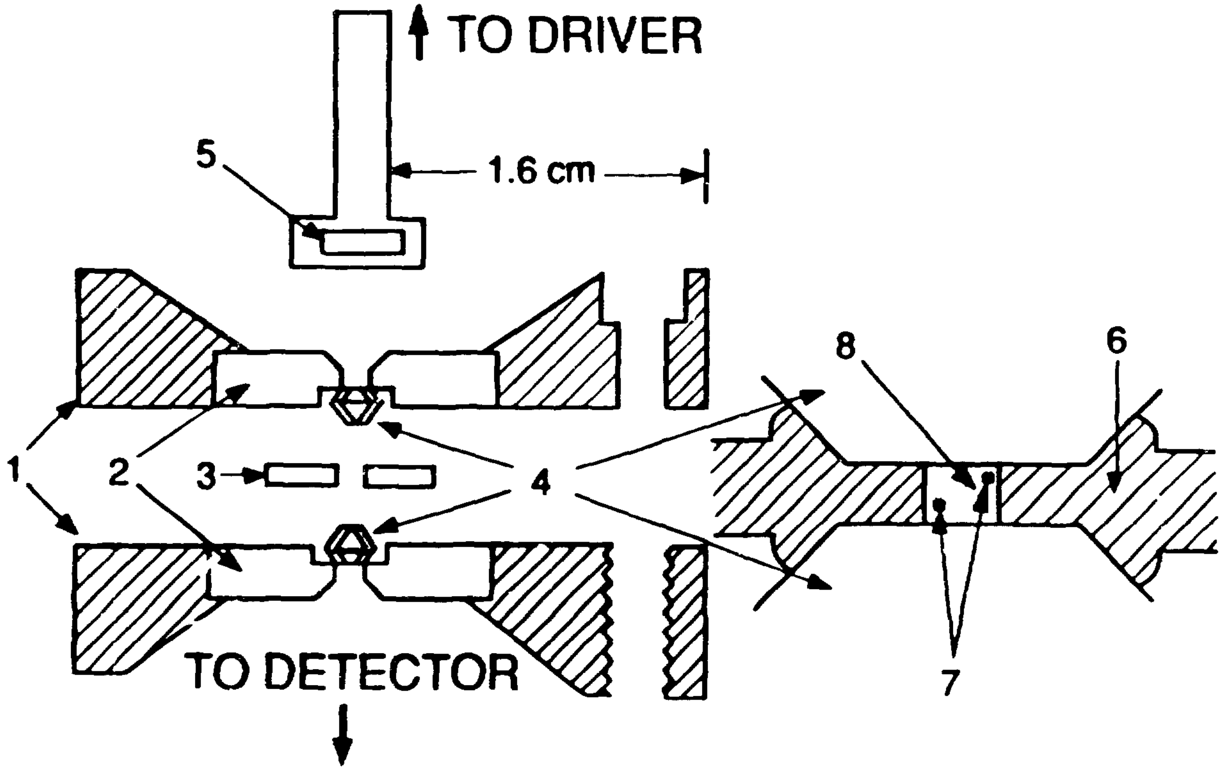
Fig.5 The proposed high-pressure structure (HP1) for GeI_4 (SnI_4). It is composed of randomly oriented $(GeI_4)_n$ chains with GeI_4 as the molecular building block and n increases with pressure increase. Each molecule has two bridging I_b and two singly bounded I_s iodides. The molecules are linked via the I_b and the charge localization is via the $\cdots Sn \cdots I_b \cdots I_b \cdots Sn \cdots$ path.

Fig.6 The proposed scheme for the second structural phase HP2. A complete molecular association takes place and charge delocalization is thre-dimensional. This structure is unique to GeI_4 and has not been observed in SnI_4 to pressures of 35 GPa.

Fig.7. The temperature dependence of the magnetic hyperfine interaction in $Ni^{129}I_2$ at P = 6.7 GPa (T_N = 150 K). The saturation hyperfine field H_{hy}^{sat} = 267 KOe. The solid line is a theoretical curve derived from a least-squares-fitting. At each pressure T_N was derived by extrapolating $H_{hy}(T)$ to zero. The upper spectrum is measured in the paramagnetic state.

Taylor and Pasternak, Stanford Workshop, FIGURE # 1





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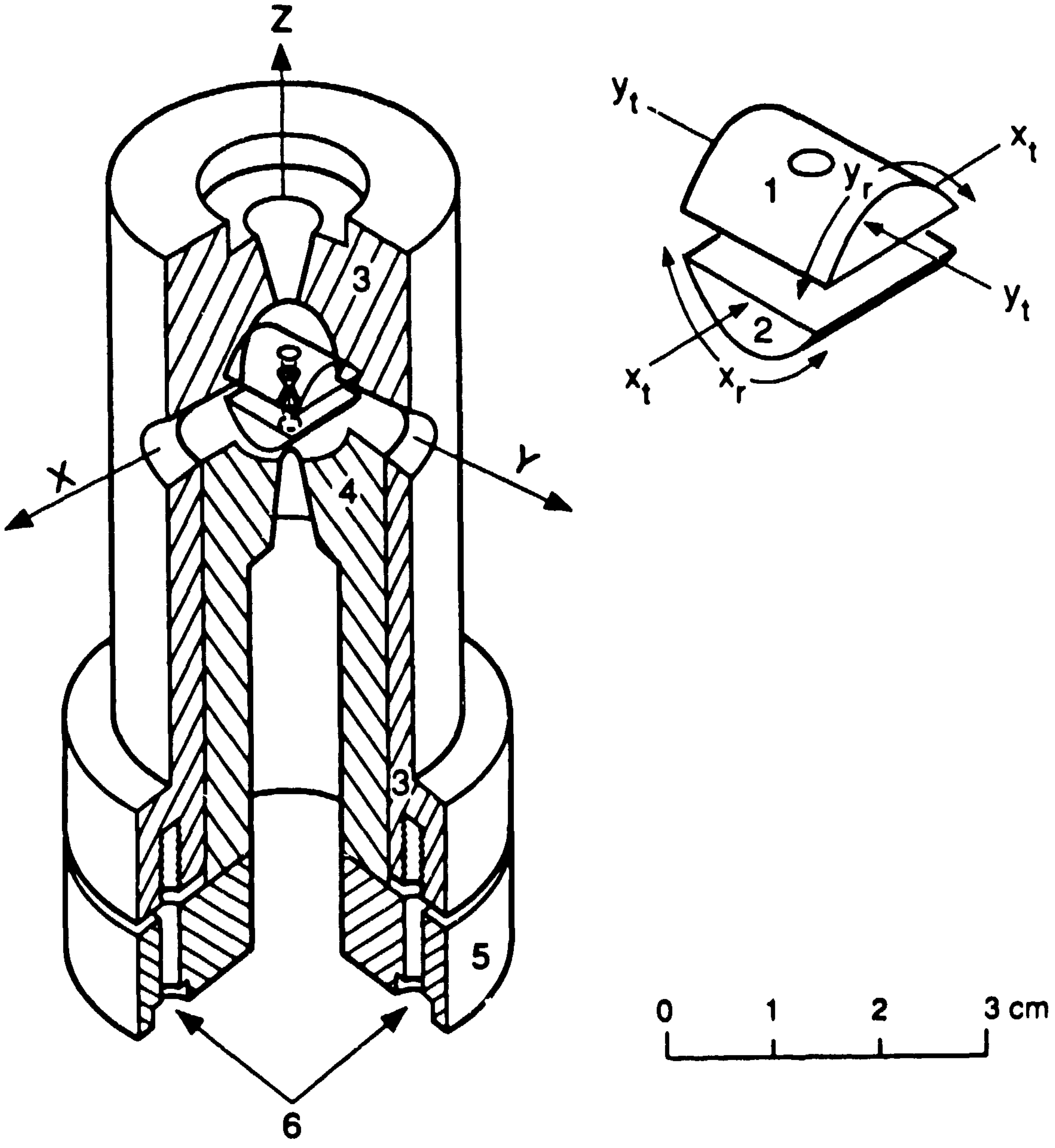
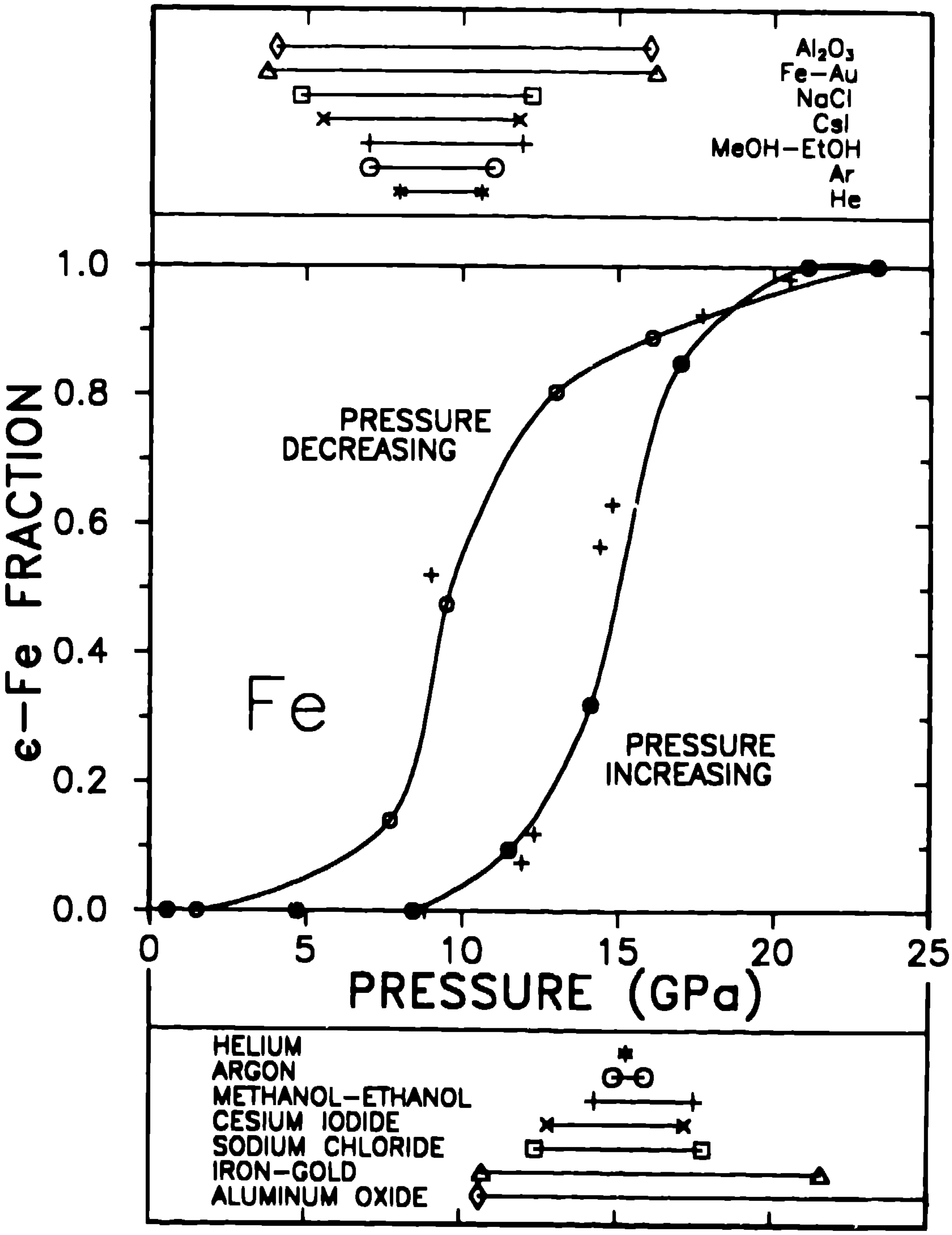
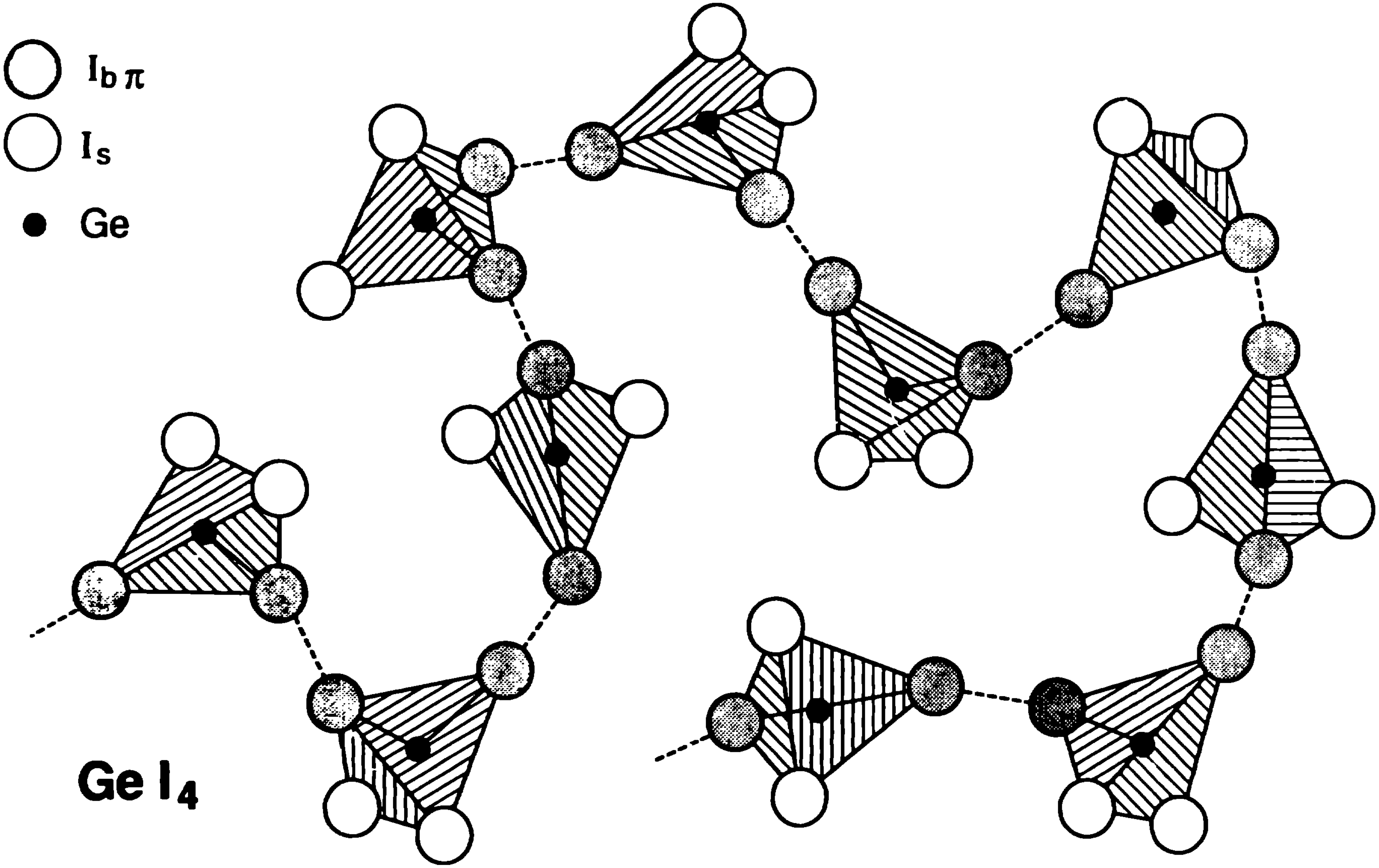
Taylor and Pasternak, Stanford Workshop, FIGURE # 3



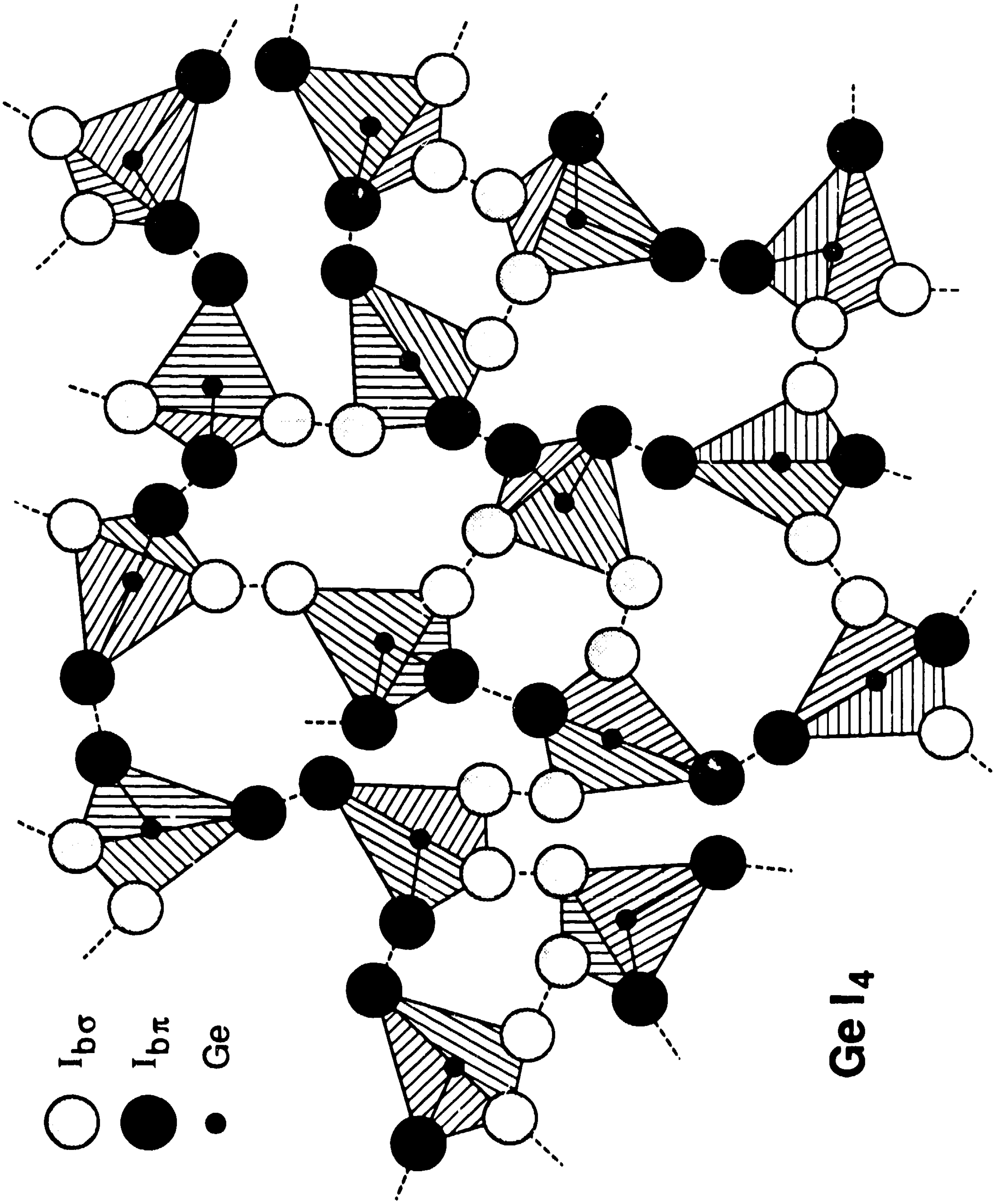
Taylor and Pasternak, Stanford Workshop, FIGURE # 4





Taylor and Pasternak, Stanford Workshop, FIGURE #2

Taylor and Pasternak, Stanford Workshop, FIGURE #6



Taylor and Pasternak, Stanford Workshop, FIGURE # 7