LA-UR 91-3912

LA-UR--91-3912

DE92 005072

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405 ENG-36

TITLE MOSSBAUER SPECTROSCOPY AT PRESSURES UP TO 40 GPa

AUTHOR(S) R. Dean Taylor, P-10/LANL
Moshe P. Pasternak, Tel Aviv Univ.

SUBMITTED TO High Pressure Research
Proceedings of the XXIX Meeting of the European High Pressure Research Group (Gordon & Breach)

DISCLAIMER

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

MOSSBAUER SPECTROSCOPY AT PRESSURES UP TO 40 GPA

R. D. Taylor, P-10

Moshe P Pasternak, P-10 Consultant/Tel Aviv University

Contributed paper to be published in High Pressure Research

Submitted: November 20, 1991

LA-UR-91-

Mossbauer spectroscopy (MS) is a viable "non-contact" technique applicable to high-pressure, diamond anvil cells (DAC) with samples containing a wide variety of the elements suitable for MS.

The convenience and simplicity of diamond anvil cells as a means to obtain static high pressures even into the megabar regime has resulted in a renewed interest in pressure as a complement to the usual physical measurements. However, the required small sample size and the difficulty of communicating with the sample leave only x-ray and optical spectroscopy as the readily available tools. Mossbauer spectroscopy which involves recoil-free, low-energy γ rays, provides a powerful additional technique to study a myriad of physical properties in a DAC. MS concerns a particular isotope and can provide local information on phase changes and hysteresis, isomer shifts, valence, bonding, magnetic and quadrupolar interactions, lattice dynamics, and multiple sites. The Mossbauer effect has been seen in about a hundred isotopic transitions in about forty different elements; many are suitable for DAC-MS use, most notably ^{57}Fe, ^{119}Sn, ^{121}Sb, ^{125}Te, ^{129}I, ^{119}Sn, ^{151}Eu, ^{161}Dy, ^{197}Au, and ^{237}Np. Since the information available from MS is obtained from analyzing the precise energy profile of the Mossbauer γ ray from a source/absorber combination, no contacts or difficult coupling to the DAC are required. We review a number of salient features of the DAC-MS method and present some examples, including new work on FeI$_2$.

MÖSSBAUER SPECTROSCOPY AT PRESSURES UP TO 40 GPa

R. Dean Taylor and Moshe P. Pasternak*, Physics Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545 USA

Mössbauer spectroscopy is shown to be a viable "non-contact" technique applicable to high-pressure, diamond-anvil cells with samples containing a wide variety of the elements.

Key words: Mössbauer Effect, high pressure, diamond anvil cells

INTRODUCTION

The convenience and simplicity of diamond anvil cells (DAC) as a means to obtain static high pressures even into the megabar regime has resulted in a renewed interest in pressure as a complement to the usual physical measurements. However, the required small sample size and the difficulty of communicating with it leave only x-ray and optical spectroscopy as the readily available tools. Mossbauer Spectroscopy (MS) which involves recoil-free, low-energy γ rays affords a powerful additional technique to study a myriad of physical properties in a DAC. MS concerns a particular isotope and can provide local information on phase changes and hysteresis, isomer shifts, valence, bonding, magnetic and quadrupolar interactions, lattice dynamics, and multiple sites. The Mossbauer effect has been seen in about a hundred isotopic transitions in about forty different elements[1]; many are suitable for DAC-MS use, most notably ^{57}Fe, ^{119}Sn, ^{121}Sb, ^{125}Te, ^{129}I, ^{129}Xe, ^{149}Sm, ^{151}Eu, ^{161}Dy, ^{197}Au, and ^{237}Np. Since the information available from MS is obtained from analyzing the precise energy profile of the Mossbauer γ ray from a source/absorber combination, no contacts or difficult coupling to the DAC are required. Many aspects of MS in DAC have been presented before[2-5]; we will review here a few salient features of DAC-MS and present some examples, including new work on FeI_2.

EXPERIMENTAL

Most of the MS to date has been carried out in modified Merrill-Bassett cells[5]; a miniature version of this type has also been used[6]. Usually a Mossbauer absorber sample is placed in the DAC with ruby chips for ruby-fluorescence pressure measurements[7] and argon as a pressurizing medium. Pressurized radioactive source experiments have the appeal that the γ rays are attenuated by only one diamond anvil, a consideration for the 14.4-keV γ ray of ^{57}Fe. For absorber experiments the gasket doubles as a collimator to block the bulk of the source beam not passing through the sample. Geometrical effects are important for efficient counting; a typical MS schematic is shown in Fig.1. The relative areas and the spacings of the source, the sample, and the detector affect the count rate and the magnitude of the Mossbauer resonance. For a few cases, *e.g.* ^{57}Co, the Mossbauer parent (source) is available with a high enough specific activity to allow a near-point-source, close-by configuration and a significantly reduced nuisance background. A sample thickness optimized for MS often requires the use of enriched isotopes to overcome the deleterious effects of electronic absorption.

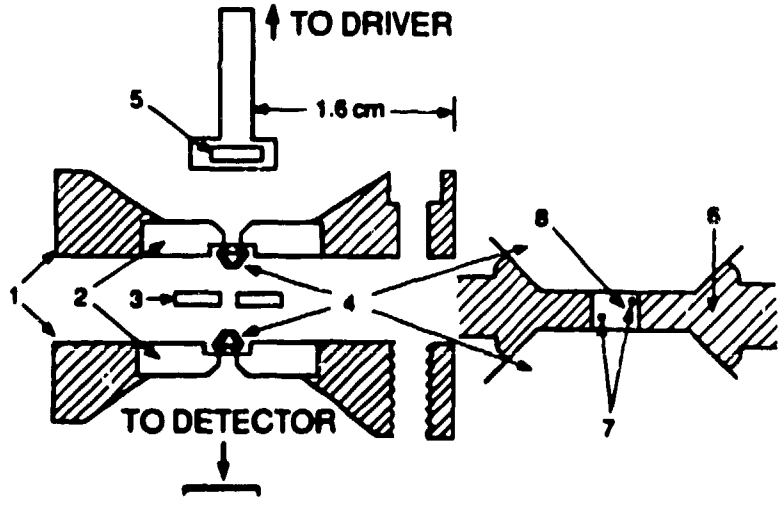

Figure 1. Schematic of MS-DAC: (1) Platens with three closure screws, (2) anvil backing plates, (3) high-Z material gasket, (4) diamond anvils, (5) MS source on Doppler driver rod, (6) enlarged view of gasket showing precompression and sample region, (7) ruby chips, and (8) MS absorber sample in pressurizing medium.

EXAMPLES

Epsilon Iron

Iron metal sluggishly transforms at room temperature from a bcc- to a hcp-phase, starting near 10 GPa. The hcp ε-Fe is not magnetic whereas the bcc α-Fe is; the well known six-line magnetic hyperfine Mössbauer spectrum of α-Fe is shown in the lowest part of Fig.2. As the pressure is raised a single line near zero Doppler velocity appears due to nonmagnetic ε-Fe. By 23 GPa the α-Fe is gone. The transition is equally sluggish upon reducing the pressure, and a large hysteresis associated with pressure changes is observed[7]. Both ^{57}Co in Fe sources and ^{57}Fe absorbers show the same behavior with pressure. A correlation has been suggested between a wide range of onset-completion pressures of the α⟷ε transition and the nature of the pressurizing medium used[8], but we note that the width of the hysteresis loop at equal concentrations of α- and ε-Fe is always 6.2 ± 0.2 GPa[7].

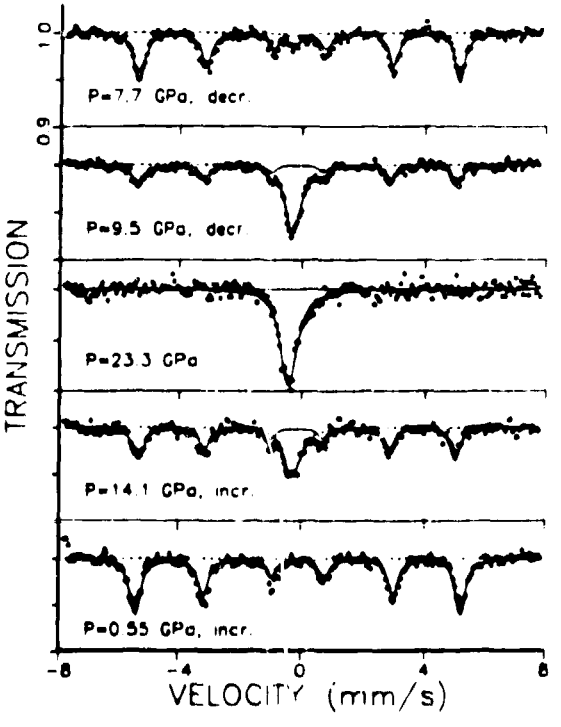

Figure 2. Mössbauer spectra at room temperature of Fe metal as a function (from bottom) of increasing, then decreasing pressure showing the α⟷ε transition and a large pressure hysteresis.

Mott Transitions

We have reported ^{129}I MS results on the pressure induced insulator-metal Mott transition in NiI_2[9,10] and CoI_2[10]. MS was used to follow the isomer shift, the induced saturation hyperfine field, and the Neel temperature T_N as a function of pressure. In both cases T_N rose dramatically until at a critical pressure P_c the magnetism disappeared in the non-correlated metallic state (the Mott transition). For NiI_2 T_N went from 75 to 310K at P_c = 19 GPa. For CoI_2 T_N rose from 11 to 125K near P_c = 13 GPa. The MS of ^{129}I also provides a determination of relative orientation of the principal axes of the electric field gradient and the magnetic field.

Preliminary ^{129}I MS with pressure on FeI_2 shows a similar behavior, *i.e.*, T_N rises rapidly with pressure; metallization has not yet occurred at 60 kbar. A room temperature ^{57}Fe Mossbauer spectrum in the same sample at P = 60(2) kbar is shown in Fig.3. We were able to obtain ^{57}Fe Mossbauer spectra despite a 4-mm total thickness of diamond and severe attenuation of the 14.4-keV γ ray

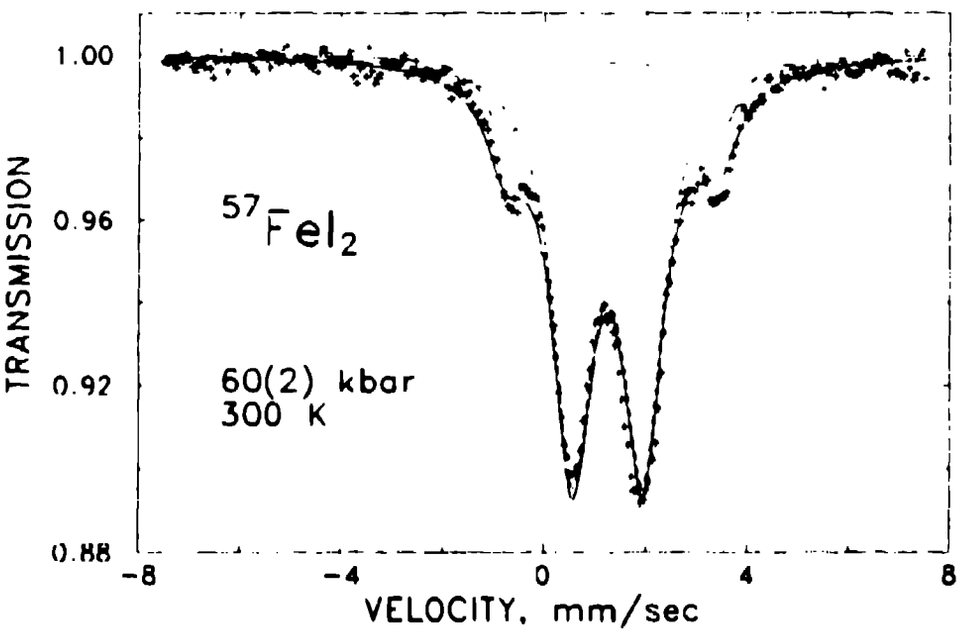

Figure 3. ^{57}Fe Mossbauer spectrum at room temperature of FeI_2 at a pressure of 60 kbar fit with two symmetric doublets (dashed lines). The inequivalent sites each have about the same isomer shift, but quadrupole splittings differing by a factor of 3.0 (see text).

by the iodine; we credit the 0.5-mm "point source" of ^{57}Co in Rh together with the inherently high recoil-free fraction of ^{57}Fe MS. ^{57}Fe absorber MS in DAC is easier than one might believe. The spectrum was fit assuming two sites, each quadrupole split. At this time the origin of the 17 percent site is unclear, but it does seem to be a consequence of the pressurization and not an impurity. ^{57}Fe MS at other temperatures and pressures should clarify the situation.

ACKNOWLEDGMENT

This work was supported in part by a grant from the LANL Institute of Geophysics and Planetary Physics.

REFERENCES

* Permanent address: School of Physics and Astronomy, Tel Aviv University, Ramat Aviv 69978, Israel

1. N. N. Greenwood and T. C. Gibb, *Mossbauer Spectroscopy* (Chapman and Hall Ltd.,London, 1971)
2. A. Jayaraman, *Rev. Mod. Phys.*, 55, 65 (1983)
3. M. Pasternak and R. D. Taylor, *Hyp. Int.*, 47, 415 (1989)
4. R. D. Taylor and M. P. Pasternak, *Hyp. Int.*, 53, 159 (1990)
5. M. P. Pasternak and R. D. Taylor, *Hyp. Int.*, 62, 89 (1990)
6. E. Sterer, M. P. Pasternak and R. D. Taylor, *Rev. Sci. Inst.*, 61, 1117 (1990)
7. R. D. Taylor, M. P. Pasternak and R. Jeanloz, *J. Appl. Phys.*, 69, 6126 (1991) and references therein.
8. N. von Bargen and R. Boehler, *High Press. Res.*,6, 133 (1990)
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. M. P. Pasternak, R. D. Taylor and R. Jeanloz, *J. Appl. Phys.* to be published.