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HIGH PRESSURE MAGNETISM

R. Ingalls

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Abstract.—A study of the Mössbauer effect of $^{57}$Fe in magnetic materials subjected to high pressures is described. Specific systems reviewed are FeF$_2$, α, ε and γ phases of iron, invar, stainless steel and a metallic glass.

1. Introduction.—Especially since P.W. Bridgman’s pioneering work with high pressures has the capability to vary interatomic spacing significantly enhanced the study of matter /1/. Perhaps the most striking aspect of such work is one’s ability to induce crystallographic, magnetic, or electronic phase changes with high pressure. Thus, for example, cubic materials can be made hexagonal, ferromagnetic made paramagnetic, and insulating made conducting. In many instances the new structures or phases that appear may only be stable at high pressure, while in other cases they may persist after the pressure is released. Even where new phases, per se, are not generated by high pressures, material properties may still be significantly altered, since a variation of the interatomic spacing affects energy levels in matter. In particular, optical, X-ray and even γ-ray energies have been observed to have a pressure dependence. Moreover, such a dependence is fundamentally related to our microscopic understanding of materials.

The first Mössbauer experiment at high pressure, by R.V. Pound et al. /2/, was a precision study of the isomer shift of metallic iron to a pressure of 3 kbar. This was soon followed by an extensive research program by H.G. Drickamer /1/ and coworkers, mainly with the isotope $^{57}$Fe, but to pressures which were as much as two orders of magnitude higher. This began with an extension of the above work on b.c.c. iron (α-Fe) /3/ and then on to dilute iron alloys /4/ and iron compounds /1/, with special emphasis on the isomer shift. The basic pressure-induced decreases in isomer shift (increase in $\delta^2(0)$) observed in virtually all $^{57}$Fe systems, seems quite predictable in the metallic systems. There the main effect is a compression of the 4s-like conduction electron charge density, almost as if it were due to free electrons /5/. Theoretical treatments have verified this feature /6/.

The isomer shift in iron compounds and its pressure dependence has a more complex interpretation and has prompted a large effort in molecular orbital calculations /7,8/. The basic feature is the importance of the covalent 4s admixture and overlap contributions from the ligands as well as, in some cases, back donation of 3d electrons from the ligands. Pressure work here has been instrumental in obtaining a satisfactory calibration constant, α, defined by /5/

$$I.S. = \alpha \cdot \delta^2(0) + \text{const}.$$ 

More recently, high pressure studies have been made on many other Mössbauer isotopes /9/.

Compared with pressure studies of the other Mössbauer parameters, it is probably fair to say that the isomer shift work has given us the most hard information for comparison with theory, to date. Yet, the other parameters are certainly sensitive to pressure as well, i.e., recoilless fraction, second-order Doppler shift, quadrupole splitting and, of course, the magnetic hyperfine splitting. The latter is the topic of this paper. Because of length limitations, here we mainly review some of the $^{57}$Fe work performed in our laboratory at the University of Washington.

In contrast to the isomer shift studies reported above, the pressure dependence of the hyperfine field has not shed as much light on the relevant nuclear calibration constants, e.g., the magnetic moments of the Mössbauer levels. Instead it has drawn us very deeply into questions involving the origin of magnetism in solids, and the effect
of pressure on this magnetism. Historically, as a basic thermodynamic variable, pressure has played a secondary role to the magnetic field strength, \( \mathbf{H} \). Of course pressure may be used to produce new magnetically interesting phases, but its main use here is in its effect upon magnetic critical temperatures and magnetization, \( M \) (usually at \( \mathbf{H} = 0 \)). A complete description of any magnetic system should, as a matter of principle, include the pressure.

The hyperfine magnetic field, \( H_{hf} \), generally provides a measure of the magnetization, or sublattice magnetization in the case of an antiferromagnet. This is because, in large part, the main contribution to \( H_{hf} \) is the contact spin density which is polarized by the same magnetic electrons that give rise to the magnetization. Most of the other contributions also go as the net spin of the magnetic electrons. This is not true of the orbital term, however. Because of unquenched orbital angular momentum in for example Co\( \text{oxygen} \)/10/, the hyperfine field decreases at low temperature in contrast to the sublattice magnetization. Thus one may say the "factor of proportionality" between \( H_{hf} \) and \( M \) is somewhat dependent upon temperature and pressure /11/. Time dependent effects such as electronic relaxation or superparamagnetism may also give rise to situations in which there is a hyperfine field and no magnetization or vice versa.

Nevertheless, the presence of a magnetic hyperfine splitting generally signifies a state of long range magnetic order. For this reason the Mössbauer thermal scan technique /12/ may be used with advantage in determining the onset of such a state. It relies on the general fact that the \( \gamma \)-ray transmission through a Mössbauer absorber changes discontinuously if either the source or absorber, moving at some constant velocity (such as zero) with respect to the other, undergoes a magnetic transition. We have found this to be a rather effective means of observing the variation of magnetic transitions with pressure.

2. Experimental.– The high pressure methods used here are closely related to those of Drickamer and co-workers /3,13/. The sample film or foil is embedded upright in a gasket of \( B + LiH \) which is placed between the truncated tips of tapered tungsten carbide pistons (Bridgman anvils). The radiation then passes radially through the gasket, perpendicular to the piston axes. As originally used, the tapered portions of the pistons were supported as well. In such a case, the pistons are generally called "Drickamer anvils" in fond tribute to their designer.

We have subsequently incorporated the above high pressure technology into a low temperature apparatus in which the force on the pistons is mutually orthogonal to the cold finger of a helium cryostat as well as the direction of the radiation /14/. Until quite recently, solid angle limitations in this design made it only feasible to apply pressure to the Mössbauer source. However, in the case of thermal scans it was possible to also squeeze absorbers for which a Mössbauer resonance line in the paramagnetic state happened to overlap the source line at zero relative velocity /15/. In such an arrangement the source is placed directly behind the magnetic absorber and both are placed under pressure. The emitted radiation is then simply recorded as a function of temperature.

In a subsequent modification, Bridgman anvils, that is, anvils without a supported taper, have also been used to study either Mössbauer sources or absorbers. When an absorber is to be studied, a moving source may be brought into the low temperature region close to the absorber (Fig. 1), as in the earlier room temperature design /13/. This development is accomplished by means of a bellows in the cryostat wall (C.M. Liu and R. Ingalls, Rev. Sci. Instrum. 49 (1978) 1680). Such arrangement requires a certain amount of care in collimating the radiation and positioning the moving source relative to the absorber.

Fig. 1: Schematic diagram of the three-axis arrangement for simultaneously applying pressure and cooling a Mössbauer absorber.

With great care in loading such cells, the sample pressure, for a given applied force, is quite reproducible. Pressure calibration may be checked by measuring electrical resistances discontinuities
of, for example, bismuth, which is loaded in a geometrical arrangement similar to that of the Mössbauer sample.

Many other high pressure techniques have been developed, some of which are based on an axial arrangement in which the γ-rays pass through anvils made of a material of low atomic number. Suitable materials are boron carbide, cubic boron nitride, or diamond. Recently, workers at the U.S. National Geophysical Laboratory, using diamond anvils, claim to have reached a static pressure of 1.72 megabar /16/. At the same institution have been Mössbauer experiments on Fe₂O₃ and Fe₃O₄ to about 600 kbar /17/. One great advantage of the diamond technique is that the pressure may be continuously monitored by observing the shift in wavelength of a fluorescent material, such as ruby, contained in the gasketed region between the anvils /18/.

3. Superexchange interaction in FeF₂.— From the early work of Abragam and Boutron /19/, and Wertheim /20/, FeF₂ has been of fundamental interest to Mössbauer spectroscopists. As one of the more ionic of the transition metal systems its temperature dependent quadrupole splitting has a rather simple phenomenological interpretation based upon simple crystal field theory /21/. The same may be said of the anisotropy constants, D and E, and g factors appearing in its spin Hamiltonian.

An attempt at a more fundamental interpretation of both the effect of temperature and pressure /22/ on this quadrupole splitting was subsequently made. This was a configuration-interaction molecular orbital calculation /23/. It has recently been refined and also used to theoretically determine the important pressure dependence of the isomer shift as well /18/.

At atmospheric pressure FeF₂ is antiferromagnetically ordered below 78 K. Moreover, it is presumably a good example of a "localized" magnetic system, with the magnetic properties completely dominated by the superexchange interaction between a Fe²⁺ ion at the center of a unit cell and a second at the corner. Although Silva's calculation /23/ of this interaction was not complete he estimated that it would increase according to Bloch's "10/3 rule" /24/. That is

\[ \gamma_J = \frac{3J}{3kN} \approx \frac{10}{3} \]

Dr. García, of our laboratory, has very recently refined this analysis /25/ by adapting a formalism developed by Rimmer /26/. In this detailed calculation, the above superexchange coupling parameter, J, consists of several terms. These include the dominant kinetic exchange term of Anderson /27/, as well as several smaller terms. The calculation was largely based upon covalency parameters of Silva /23/, plus additional overlap and transfer integrals. All were calculated as a function of pressure based upon pressure dependent X-ray data of Christoe and Drickamer /22/.

In performing this calculation it was discovered that the exchange integral, as calculated, was very sensitive to the relevant rather poorly known covalency parameters, and was easily overestimated by as much as a factor of five! However, the parameter, \( \gamma_J \), was, by way of contrast, quite insensitive to the values of the covalency parameters. García's best value is \( \gamma_J = 3.5 \).

An experiment was conducted to measure the pressure dependence of this Nb₅₁ temperature /15/. At that time it was not possible to study the complete Mössbauer spectra of absorbers in our apparatus. However in this fortuitous case it was possible to perform the thermal scan measurements as described in section 2. This was because, fortunately, at low temperature (P < 50 kbar) a stainless steel source nicely overlapped one of the lines of the quadrupole doublet in FeF₂ at \( n = 80 \) K. The experimental result was that \( T_N \) increased by 0.27 ± 0.03 K/kbar, or

\[ \frac{\Delta T_N}{\Delta N} = 3.2 \pm 0.3 \]

Since \( T_N \) is expected to go as \( J \), this result is quite consistent with the other results.

As a sidelight on the above, there have been estimates of the effect of pressure on the anisotropy constants, spin-orbit coupling, g factors, hyperfine magnetic field and quadrupole splitting below \( T_N /28/). With the recent modification of our apparatus to handle absorbers, we shall soon perform the required Mössbauer studies.

4. α and β iron.— In an extension of the earlier work on iron /2,3/ it has been learned that the pressure induced decrease in hyperfine field is essentially the same at 82 K and 20 K as at room temperature /29/. Such a decrease has been attributed in part to an enhancement of the contact density of the conduction electrons which are polarized oppositely to the core /6/. The saturation magnetization itself has been found to decrease even more rapidly than the hyperfine field /30/. This is another example where the two fields are
not strictly proportional. It may be added that the Curie temperature is independent of pressure. These results lend some support to the picture of a iron behaving much like a moderately weak itinerant magnet. (A very "weak" system would be one that barely satisfies a criterion for magnetic ordering to occur. Invar or ZrZn may be such examples /31/.)

We and others have also cooled the h.c.p. form of iron (\(\gamma\)-Fe), which is stable above 110 kbar at room temperature /3,29,32/. No magnetic ordering (i.e., no hyperfine magnetic splitting) was observed down to 2.2 K. This has been interpreted as agreeing with an itinerant picture /33/. That is, the band structure for this system apparently yields a density of states that is too low to satisfy the Stoner-Wohlfarth criterion for magnetic stability.

\[ \frac{\partial T_N}{\partial P} = -0.5 \text{ K/kbar} \]

Although the theoretical interpretation of such a result is not available, several remarks may be made. The Néel temperature of the present system is not greatly different from extrapolations based upon \(\gamma\)-Fe-Mn and \(\gamma\)-Fe-Ni-Cr alloys /35/. Moreover, since band calculations /36/ successfully predict antiferromagnetism to occur for \(\gamma\)-Fe (as opposed to ferromagnetism in \(\alpha\)-Fe) we presume that a result may be obtained in pure \(\gamma\)-Fe. A question may arise connected with the reduction of the Néel temperature with particle size at P = 0. Several causes have been suggested for such a reduction /34/ such as copper contamination, changes in the lattice parameter or strain effects. In addition there is the possibility of superparamagnetism (D.L. Williamson, private communication). In general, however, it is doubtful that any of these causes could alter our general conclusion: pressure apparently weakens the antiferromagnetic state of \(\gamma\)-Fe. However, the degree to which it is weakened may conceivably indeed be dependent upon particle size, etc.

It may also be mentioned that the Néel temperature of \(\gamma\)-Fe fits in with the dependence of \(T_N\) upon lattice parameter in a series of \(\gamma\)-iron alloys /35/. In the incommensurate systems, \(\gamma\)-FeMn and Cr, pressure also reduces \(T_N\). However, so far there is no theory to say, for example, that \(\gamma\)-Fe behaves like a "weak" itinerant system just because of the negative pressure derivative of \(T_N\).

\[ \text{Fig. 2: Thermal scans obtained at various pressures for absorbers of } \gamma\text{-Fe precipitates in a copper matrix. The fixed source is Co-57 in rhodium.} \]

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It should be remarked that the ferromagnetism in invar has prompted welcome theoretical interest /31,39/ in terms of the itinerant picture. However, a phenomenological localized description may also be made /37/. Perhaps magnetic interactions between atom pairs, at least in the sense of Moriya /40/, has validity.

Two materials which are stable antiferromagnets at atmospheric pressure are the stainless steels type 302 (% Fe76Ni12Cr1~) and type 310 (% Fe59Ni12Cr20). We have also studied them using our thermal scan method. The respective \( P = 0 \) Néel temperatures are 58 K and 31 K. The type of antiferromagnetic ordering is identical with that of \( \gamma \)-Fe. At very high pressures we find the Néel temperature of S.S. 302 to increase greatly as with the invars /38/. However, at low pressures its behavior has not been clearly measured, it may even somewhat decrease. The Néel temperature of S.S. 310 clearly decreases with pressure in the low pressure region (\( P < 50 \) kbar) as with \( \gamma \)-Fe (C.M. Liu and R. Ingalls, J. Appl. Phys., to be published). As with the latter we have not gone to very high pressures. Here again as with the invars, increasing Fe content stabilizes the antiferromagnetic state, and the more stable the system, antiferromagnetically, the more stable it is with pressure. However, more information is required to give a complete picture of these systems.

7. Iron metallic glasses.—Very recently we have begun a study of ferromagnetic metallic glasses containing iron. They are not only interesting technologically because of their low coercivity, etc., but also theoretically, where they appear to be good examples of ideal weak itinerant ferromagnets /41/.

Using absorbers of amorphous \( \text{Fe}_{73}\text{Ni}_{18}\text{Cr}_{9} \) (METGLAS 2826 A, Allied Chemical) we have measured the Mössbauer effect and its dependence upon pressure (C.M. Liu, R. Ingalls J.E. White, K.V. Rao, and S.M. Bhagat, J. Appl. Phys. to be published). Above the Curie temperature, 245 K, the \( P = 0 \) spectrum is a broad, asymmetric doublet, presumably caused by a range of isomer shifts and quadrupole splittings. At 78 K, well below \( T_c \), the spectrum consists of this same doublet superposed on a diffuse hyperfine pattern. From the overall width of this magnetic component we estimate the largest significant hyperfine field to be approximately 210 kOe. The intense para magnetic component below \( T_c \) is unique for a metglas. However, such a feature is not surprising in view of the observation of a large, low temperature high field, susceptibility for the same material /42/.

The pressure dependence of this system to 110 kbar is very similar to the ferromagnetic invar alloys discussed earlier. The Curie temperature reduces at an approximate rate of \( \sim 0.5 \) K/kbar, while the hyperfine field initially decreases at a rate of \( \sim 1 \) kOe/kbar. At higher pressures the rate of decrease is smaller. Work on this and other similar intriguing systems is continuing.

8. Summary.—The Mössbauer effect is an extremely powerful tool for observing the pronounced effects of pressure on a large variety of magnetic systems. However, at present, experiments in this field remain demanding. But the same may be said for the theory of magnetism itself especially at finite temperatures. Regretfully, to make things worse, most such calculations fail to include pressure (or volume) in a fundamental way, although the measured pressure behavior is a potential verification of their validity. Optimistically, it is hoped that at some point in the near future the theoretical advances, can begin to keep pace with the experimental progress!

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