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Mössbauer and Nuclear Magnetic Resonance Studies of Several Iron Phosphides[1]

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The Fe^{57} Mössbauer spectra of three iron phosphides—FeP, Fe_2P, and Fe_3P—and the P^{31} nmr spectrum of FeP have been determined over a wide range of temperatures. The ferromagnetic compounds Fe_2P and Fe_3P show complex hyperfine splitting of their Mössbauer spectra. The observed hyperfine field is correlated with the crystallographic environment of the different iron sites. Bonding in these iron phosphides apparently involves donation of electrons from phosphorus to the iron d bands, reducing their magnetic moments and hyperfine fields. The Mössbauer and nmr spectra of FeP indicate an electronic rearrangement with change of temperature.

Metallic iron and red phosphorus react readily at elevated temperatures (700–1000°) to form four well-defined compounds, Fe_3P, Fe_2P, FeP, and FeP_2. The compounds become less metallic with increasing phosphorus content, but all except FeP_2 show metallic conductivity. Their crystal structures[2-4] and bulk magnetic properties[5-8] have been studied previously but their magnetic structures were unknown. We have used Mössbauer spectroscopy to study their magnetic properties in greater detail. The three metallic iron phosphides might be expected to have similar bonding and are especially interesting because of the wide range of coordination numbers present. Thus the number of nearest neighbor phosphorus atoms varies from 6 to 2 in the series of compounds included in this work.

The Mössbauer effect offers an efficient method for examining the magnetic structure and bonding of iron compounds. The hyperfine splitting of the nuclear energy levels by a magnetic field at the nucleus as shown by the Mössbauer effect gives a direct measure of the magnetic field at different sites in the crystal lattice. It is not certain how the hyperfine splitting is related to the magnetic moment in all compounds, but calculations by Duncan and Golding,[9] who used the functions of Abragam *et al.*,[10] indicate a field of about 125 koersteds per unpaired 3d electron in the iron atom. Experimental results on iron compounds are in approximate agreement with this value, varying from 100 to 170 koersteds/μ_B in those cases where bulk magnetic measurements or neutron diffraction data are available for comparison.

In addition to magnetic splitting of the Mössbauer spectrum, one also observes an isomer shift indicating changes in the s electron density. As the s electron density increases at an iron nucleus, its isomer shift decreases in direct proportion. In addition, the d electrons indirectly affect the isomer shift by screening the s electrons from the nucleus, so that for iron an increase in d electrons causes an increase in the isomer shift.

Mössbauer studies of a number of ferromagnetic iron compounds with other light elements have been carried out to investigate their bonding and magnetic structures. Some of the compounds which are most closely related to the present work are FeB, Fe_2B,[11,12] Fe_4N,[13] FeSi,[14] Fe_3Si (and more dilute alloys),[15-17] and Fe_3Al.[18,19] Their Mössbauer spectra and magnetic properties have been explained by assuming electron donation from the nonmetals to the d bands of the iron atom, decreasing its magnetic moment and hyperfine field. However, although the bonding in iron–silicon and iron–aluminium alloys has been the subject of extensive research, the electronic structure of these compounds is still unclear. Several of the compounds listed above have been examined by neutron diffraction with general agreement between the Mössbauer and diffraction results.[12-16]

Experimental Section

The iron phosphides FeP, Fe_2P, and Fe_3P were all prepared by heating iron powder reduced by hydrogen with a stoichiometric amount of reagent grade red phosphorus in evacuated, sealed silica tubes for at least 24 hr at 1000°. The gray product was powdered and either used directly from the initial reaction or resealed under vacuum and heated for another 24 hr to ensure homogeneity. The addition of a trace of iodine to the sample for the second heating caused the growth of larger crystals (<0.1

(1) Parts of this paper were presented at the Organometallic and Coordination Chemistry Symposium at the Third National Royal Australian Chemical Institute Meeting in Canberra, Australia, Aug 1966, and at the International Conference on Hyperfine Nuclear Spectroscopy in Wellington, New Zealand, Oct 1966.

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mm^3). In the Mössbauer spectra observed for samples treated in these different ways there was no detectable difference from the original product. The samples were examined as crushed powders held in a plastic holder with Sellotape. For work at elevated temperatures, a mica sample holder (which could be heated in a simple tube type of furnace) was used.

X-Ray powder diffraction patterns for the products using Fe Kα radiation showed only the expected diffraction peaks for the products.[20] No lines which could be assigned to likely impurities (*e.g.*, $FePO_4$, α-iron) were visible. Titrimetric analyses of the iron phosphides were performed using potassium dichromate after solution in hot perchloric acid. *Anal.* Calcd for FeP: Fe, 64.3. Found: Fe, 63.65. Calcd for Fe_2P: Fe, 78.3. Found: Fe, 75.5. Calcd for Fe_3P: Fe, 84.6. Found: Fe, 82.0. The starting iron powder may have contained about 2% oxygen which might have formed phosphate in the course of the reaction with phosphorus.

Mössbauer spectra were obtained on a spectrometer built following the design of Whitfield and Vickerman[21] using an RIDL Model 34-12B, 400-channel analyzer driven in the time mode by pulses from a Philips GM 2314 pulse generator. The source drive was made from two Magnetic Specialities Products 12 PQ loudspeakers with a Lucite tube linking the two loudspeakers. The source was 2-mcurie Co^{57} plated on copper. It was driven sinusoidally by a Hewlett-Packard 202-A low-frequency function generator, which also fed a synchronizing pulse once each cycle into a gating circuit on the analyzer. A thallium-doped sodium iodide scintillation crystal incorporated into an RIDL counting head was used as detector (in association with the analyzer discriminator) for the 14.4-kev γ rays of interest. This spectrometer has a nonlinear velocity scale, but the true velocity is easily obtained from the channel number by calculation. Velocities were standardized relative to sodium nitroprusside, using the values of Spijkerman.[22] With this apparatus, a typical compound gave about 15% absorption; stainless steel, about 23% without correction for background.

Samples were made up to contain 15–25 mg of natural iron/cm^2. The data were treated using ALGOL computer programs developed by Hudson[23] to fit Lorentzian absorption lines to the data points using the Elliott 503 computer at the Department of Scientific and Industrial Research, Wellington, New Zealand.

The phosphorus-31 nmr spectrum of FeP was determined using a Varian DP-60 nmr spectrometer operating at 15 MHz. A 10-g sample was held in a small dewar flask in the probe and heated by a hot-air loop. Resonance frequencies were measured in a constant field and compared with that of 85% H_3PO_4 (20°) by means of a Hewlett-Packard frequency counter.

Results

FeP.—The Mössbauer spectrum of the simplest iron phosphide, FeP, is a well-resolved doublet at 293°K with a quadrupole splitting $\Delta E_Q = 0.65$ (± 0.01) mm/sec and an isomer shift $\delta = 0.25$ (± 0.03) mm/sec relative to natural iron. The shift and quadrupole splitting show normal changes with temperature, δ decreasing to -0.35 mm/sec at 810°K and ΔE_Q decreasing to 0.53 mm/sec at the same temperature. The quadrupole splitting is not surprising from a consideration of the crystal structure which is of the B31 type, a distorted nickel arsenide structure.[2] The environment of each iron is a slightly distorted octahedron of phosphorus atoms and a very distorted dodecahedron of eight iron atoms (eight Fe–Fe distances ranging from 2.66 to 3.79 A).

Cooling FeP in liquid air (90°K) causes the doublet in the Mössbauer spectrum to spread, being replaced by a broad single asymmetric absorption from -0.5 to 1.2 mm/sec with a maximum at 0.8 mm/sec. The reason for this change in the spectrum is not clear as no magnetic transitions have been observed for FeP which possesses only a weak paramagnetism down to 30°K.[5] The phosphorus-31 nmr spectrum of FeP shows a single strong resonance 375 ppm downfield from 85% H_3PO_4 at 20°. Heating the sample to 88° causes the resonance frequency to drop to -550 ppm with a simultaneous decrease in the line width from 4 to 1 gauss.

Fe_2P.—The next member of this series, Fe_2P, has a more complex Mössbauer spectrum at room temperature, as shown in Figure 1. This has been resolved by computer methods into three peaks: a single peak with $\delta = 0.16$ mm/sec, and a doublet with $\delta = 0.58$, $\Delta E_Q = 0.40$ mm/sec, and the same total area as that of the first peak. This spectrum shows the presence of two kinds of iron atom, Fe_A and Fe_B, respectively. In the crystal structure[3] (hexagonal, type C22) there are known to be two crystallographically distinct iron sites, Fe_I and Fe_{II} as shown in Figure 2. Fe_I is surrounded by an approximate tetrahedron of phosphorus atoms, whereas Fe_{II} is near the base of a square pyramid of phosphorus atoms. The quadrupole-split iron (Fe_B) corresponds to the less symmetrical iron site, Fe_{II}; and Fe_A to Fe_I.

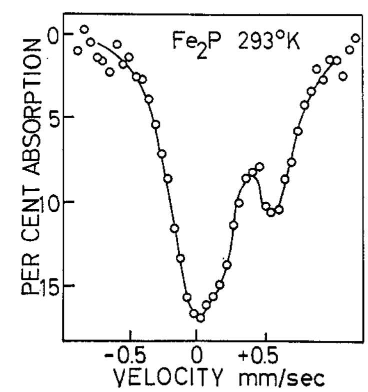

Figure 1.—Mössbauer (Fe^{57}) spectrum of Fe_2P at room temperature, 293°K.

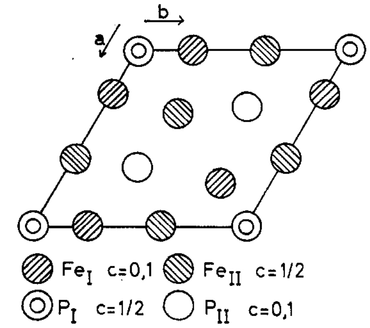

Figure 2.—Diagram of Fe_2P crystal structure after data of Rundqvist and Jellinek.[3]

(20) Fe_2P has ASTM powder pattern 2-1143. The pattern listed for FeP on file, No. 3-1066, is completely wrong but the pattern we observed agreed with those calculated from the crystal structure by Rundqvist.

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Table I

Summary of Iron Phosphide Mössbauer Data at 90°K

	Fe_2P II	Fe_2P I	Fe_3P III	Fe_3P II	Fe_3P I	Fe metal
δ, mm/sec	0.40	0.05	0.38	0.29	0.40	0[a]
H, koersteds	110	140	185	265	295	335
μ_{av}, μ_B/Fe	1.32[b]			1.84[c]		2.22[d]
H/μ, koersteds/μ_B	95			135		
μ(distributed)[e]	1.21	1.54	1.37	1.96	2.18	2.22
Nearest neighbor phosphorus atoms	5	4	4	3	2	

[a] δ of iron taken as +0.31 mm/sec relative to sodium nitroprusside. [b] See ref 6, 7. [c] See ref 6, 8. [d] E. C. Stoner, "Magnetism and Matter," Methuen and Co., London, 1934, p 366. [e] Calculated assuming H/μ is the same for the different iron sites for any given compound: μ(distributed), when combined in any compound, gives the value of μ_{av} experimentally determined.

Fe_2P has been reported to be ferromagnetic with a Curie point just below room temperature (266°K).[6,7] At 195°K the Mössbauer spectrum shows only a broad unresolved absorption, but at liquid air temperature, 90°K, the spectrum spreads into the complex pattern shown in Figure 3. This has been resolved into two overlapping spectra of six lines, one each from the two iron sites. Fe_I has a magnetic field of 140 koersteds while Fe_{II} has a field of only 115 koersteds.

In an attempt to study the P^{31} nmr of the two different types of phosphorus atoms in Fe_2P, we were unable to detect a signal in the temperature range available on our equipment (up to 100°).

Fe_3P.—The tetragonal, ferromagnetic compound Fe_3P shows a very complex Mössbauer spectrum at low temperatures as shown in Figure 4. This has been resolved into 18 lines, six from each of the three crystallographically distinct iron sites. The Mössbauer data for each of the iron sites and magnetic information derived from the data are given in Table I. As Fe_3P is heated toward its Curie temperature of 716°K, its Mössbauer spectrum shrinks without changing its appearance, showing that the Curie points of all of the iron sites are nearly the same. At 800°K its spectrum shows only a single line at δ = 0.28 mm/sec and a half-width of 0.30 mm/sec indicating little, if any, quadrupole splitting.

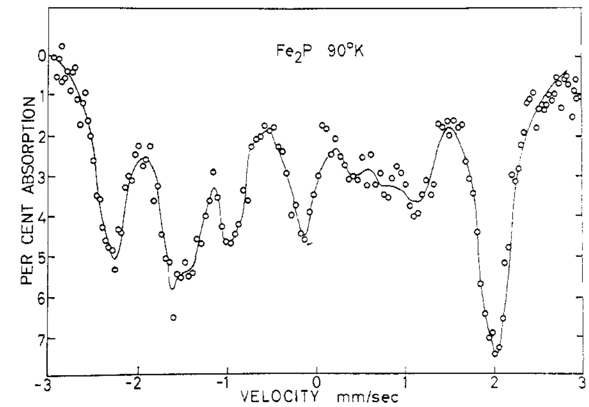

Figure 3.—Mössbauer (Fe^{57}) spectrum of Fe_2P at liquid air temperature, 90°K.

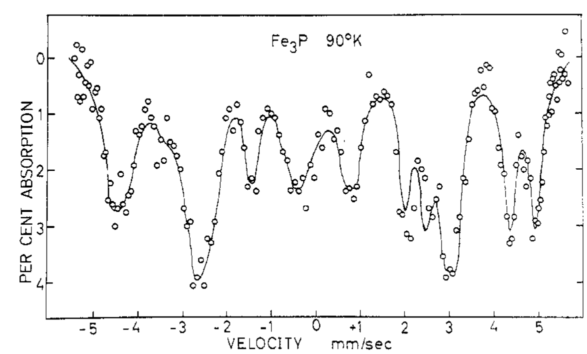

Figure 4.—Mössbauer (Fe^{57}) spectrum of Fe_3P at liquid air temperature, 90°K.

Discussion

Fe_2P and Fe_3P.—The magnetic structure of the ferromagnetic compound Fe_2P can be interpreted by assuming that the hyperfine field observed by the Mössbauer effect at the different iron sites is directly proportional to the magnetic moment at those sites. We can then apportion the observed saturation moment of 1.32 μ_B/iron[6,7,24] between the two sites to give 1.54 and 1.21 unpaired electrons for Fe_I and Fe_{II}, respectively. From the bulk magnetic properties the preferred direction of magnetization is known to be parallel to the hexagonal axis—that is, the net spins tend to line up along this axis. Thus from the distribution of magnetic moments between the two iron sites given by our Mössbauer study and assuming the moments are all parallel (it is ferromagnetic) and prefer to lie along the hexagonal axis,[7] we have determined the magnetic structure of Fe_2P. The only other technique by which this could be done is neutron diffraction which has not yet been used to study this compound.

The validity of this procedure is illustrated by the work of Shirane, *et al.*,[13] with Fe_4N where excellent agreement between the magnetic moments obtained by neutron diffraction and those found by apportioning the average magnetic moment was found (average H/μ is 110 koersteds/μ_B). The study of a number of Laves-phase compounds of the formula MFe_2 by Wallace[25] also showed a good correlation between magnetic moments and the hyperfine field with an average value H/μ of 140 koersteds/μ_B.

The magnetic properties of Fe_I in Fe_2P can be com-

(24) Because of the extreme magnetic hardness of Fe_2P containing a small amount of excess P reported by Cadeville and Meyer,[5,6] it seems likely that the magnetic saturation moment of 0.85 μ_B/iron atom reported by Chiba is too low: S. Chiba, *J. Phys. Soc. Japan*, **15**, 581 (1960).

(25) W. E. Wallace, *J. Chem. Phys.*, **41**, 3857 (1964).

pared with those of Fe_{III} in Fe_3P as shown in Table I. Each of these iron atoms has four phosphorus atoms bonded to it and should show the same magnetic field if the bonding involves donation of three electrons from each phosphorus atom. Using the law of corresponding states, that is comparing their magnetic fields at equal fractions of their Curie temperature, we observe 140 koersteds for Fe_I of Fe_2P at 90°K and 175 koersteds for Fe_{III} of Fe_3P at 240°K. The difference between these two values is taken to indicate the more metallic character of Fe_3P with several more nearest neighbor iron atoms than in Fe_2P. The hyperfine splitting of Fe_I in Fe_3P decreases with increasing temperature approximately following the Brillouin function for $J = 1$ as shown in Figure 5. Since the Brillouin function is derived from a theoretical treatment of bulk magnetization, this plot gives additional support to the assumption that the hyperfine magnetic field is proportional to the magnetic moment of an iron atom.

We propose that the bonding in Fe_2P and Fe_3P involves donation of electrons from the phosphorus to the d bands of the iron reducing their average magnetic moment from that observed in pure iron. While this is contrary to the direction expected by electronegativities, it provides a reasonable explanation of the reduced hyperfine fields and magnetic moments observed in the iron phosphides. If each phosphorus atom in Fe_2P were to contribute $^1/_3$ electron to each of its nine neighboring iron atoms, one would expect to find magnetic moments at the two iron sites in the ratio of approximately 5:4 for Fe_I and Fe_{II}, respectively. This is nearly the ratio observed between the distributed magnetic moments given in Table I. The small positive isomer shift of Fe_{II} with respect to Fe_I in Fe_2P is also consistent with the donation of electrons into the iron d band by phosphorus. In Fe_3P the more complex crystal structure makes detailed predictions more difficult, but the reduced hyperfine fields and magnetic moments again indicate donation of electrons from phosphorus to iron. This bonding scheme is analogous to that suggested for FeB, Fe_2B,[11] and Fe_4N[13] where electron transfer appears to be in the opposite direction to that expected by electronegativity.

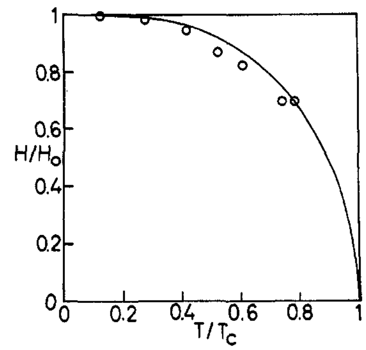

Figure 5.—Experimental points are H/H_0 of Fe_I in Fe_3P plotted against T/T_c for Fe_3P taking T_c as 716°K.[6,8] The solid line is calculated on the basis of a Weiss molecular field with $J = 1$.

FeP.—Our Mössbauer and nmr data for FeP are consistent with the band structure for the transition metal monophosphides proposed by Goodenough.[26] The decrease in nmr chemical shift with increasing temperature, although much less than that observed for FeSi,[14] may indicate some electronic rearrangement with increasing temperature. The broad asymmetric Mössbauer absorption observed at 90°K would be in accordance with a redistribution of electron density. This spectrum shows that there are at low temperatures two nonequivalent iron sites in the lattice in spite of the fact that no anomalous properties are observable either crystallographically or magnetically. At low temperatures no change in the X-ray powder pattern is observed.

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(26) Reported by Stein and Walmsley.[5]