JOURNAL OF SOLID STATE CHEMISTRY 13, 84–91 (1975)

Mössbauer and X-Ray Studies of Fe_5PB_2

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Received February 22, 1974

Mössbauer spectroscopic and X-ray crystallographic studies of the ternary compound Fe_5PB_2 have been undertaken. It is suggested that in the nonstoichiometric compound part of the phosphorus positions are occupied by boron atoms. The Mössbauer data indicate that Fe_5PB_2 is a simple ferromagnet with the tetragonal axis as the direction of easy magnetization, the moments being $\sim 1.6\ \mu_B$ and $\sim 2.2\ \mu_B$ for Fe(1) and Fe(2), respectively.

1. Introduction

In connection with Mössbauer spectroscopic studies of phosphides containing iron (*1*) we have previously examined the effects produced by substitution of boron for phosphorus in Fe_3P. In order to study the influence of the boron and phosphorus environments about iron more closely we decided to investigate the hyperfine fields acting on the iron nuclei in Fe_5PB_2.

The occurrence of Fe_5PB_2 was discovered in the course of studies of the phase relationships in the ternary system Fe–P–B (*2*, *3*), and the crystal structure was found to belong to the tetragonal Cr_5B_3 type (*2*). In the ideal structure, the unit cell contains 20 iron atoms distributed on one 16-fold and one fourfold position. The boron atoms occupy one eightfold, and the phosphorus atoms one fourfold, position. The lattice parameters for Fe_5PB_2 are variable, indicating a range of homogeneity. Magnetic susceptibility measurements (*4*) have shown that Fe_5PB_2 is ferromagnetic with a Curie temperature varying between 615 and 639 K, depending on the composition. The average magnetic moment extrapolated to 0 K was reported to be 1.73 μ_B per iron atom.

2. Experimental Details

The samples used in the present study were prepared during the course of previous work on Fe–P–B alloys by one of the present authors, and the reader is referred to (*2*) for further details. X-ray powder diffraction patterns were recorded in a Philips XDC-700 camera using $CrK\alpha_1$ radiation and silicon ($a = 5.43054$ Å) as internal calibration standard. Least-squares refinements of the unit cell dimensions were made on an IBM 1800 computer using a local program. Least-squares refinement of the single crystal structure data were made on a CDC 3600 computer using a local version of the program LALS, written by P. K. Ganzel, R. A. Sparks and K. N. Trueblood, Los Angeles, Calif.

Mössbauer transmission spectra were recorded at different temperatures in the range 80–900 K. The absorbers, containing 5–25 mg/cm^2 of iron, were pellets pressed from a mixture of boron nitride and powdered samples of Fe_5PB_2. ^{57}Co*Pd* was used as

TABLE I

PHASE-ANALYTICAL DATA FOR THE Fe_5PB_2-CONTAINING SAMPLES USED FOR RECORDING MÖSSBAUER SPECTRA

Sample No.	Phases observed in powder photographs	Fe_5PB_2 unit cell dimensions (Å)	
		a	*c*
1	$Fe_5PB_2 + Fe_2B$	5.4855(2)	10.3364(6)
2	$Fe_5PB_2 + Fe_2B$	5.4854(2)	10.3411(6)
3	$Fe_5PB_2 + FeB + Fe_2P$	5.4945(1)	10.3682(3)

source at room temperature. Least-squares fits of lorentzian lines were made to the experimental data on an IBM 370/155 computer using hyperfine fields, isomer shifts, etc., as parameters.

3. X-Ray Crystallographic Studies

As mentioned before, the Fe_5PB_2 phase has a range of homogeneity. We decided to investigate whether the changes in composition would produce any effect on the Mössbauer spectra, and we therefore studied three Fe_5PB_2-containing alloys of different compositions. The phase-analytical data for these alloys, as obtained by X-ray powder diffraction, are presented in Table I. In all three alloys the amount of the phases present in addition to the Fe_5PB_2 phase was so small that no significant contributions to the Mössbauer spectra should occur.

In order to obtain more accurate crystallographic information on the Fe_5PB_2 structure, we subjected the previously recorded single crystal X-ray diffraction data (*2*) to least-squares refinements, using the improved computing facilities currently available. As in the previous work, the six strongest (*h*0*l*) reflexions were omitted since they were obviously badly affected by extinction. In the first refinement, one scale factor, individual isotropic temperature factors for all atomic positions, positional parameters for Fe(1) and B, and occupation parameters for Fe(2) and P were varied. The Fe(1) and B positions were assumed to be fully occupied. The results were as follows. For the Fe(2) position, the deviation from full occupation was less than 0.7 standard deviations as calculated by the program. Furthermore, the isotropic temperature factors as obtained for Fe(1) and Fe(2) differed by less than one standard deviation. The occupation parameter obtained for phosphorus was 0.88(5). (In the following text, numbers in parenthesis after numerical values are the calculated standard deviations, referring to the last significant digits.)

TABLE II

RESULTS FROM REFINEMENT OF Fe_5PB_2 STRUCTURE. SPACE GROUP *I* 4/*mcm*; $a = 5.482$ Å, $c = 10.332$ Å

	x	*y*	*z*	*B*(Å^2)	*r*
16 Fe(1) in 16 *l*	0.1695(4)	[=1/2 + *x*]	0.1400(2)	0.28(2)	
4 Fe(2) in 4 *c*	0	0	0	0.30(3)	
8 B in 8 *h*	0.384(6)	[=1/2 + *x*]	0	0.43(21)	
$4(1-r)$P 4 *r* B } in 4 *a*	0	0	1/4	0.30[a] 0.40[a]	0.09(4)

[a] Not varied in least squares refinement.

TABLE III

INTERATOMIC DISTANCES (Å) IN Fe_5PB_2 (DISTANCES SHORTER THAN 3.5 Å ARE LISTED)

Fe(1)–2B	2.15(2)	B–B	1.80(6)
B	2.20(2)	4Fe(1)	2.15(2)
2P	2.332(2)	2Fe(2)	2.20(3)
2Fe(2)	2.498(2)	2Fe(1)	2.20(2)
Fe(1)	2.593(4)	4B	3.11(4)
Fe(1)	2.628(4)	4P	3.39(2)
4Fe(1)	2.880(3)	2Fe(2)	3.44(3)
Fe(1)	2.893(4)		
2Fe(1)	2.936(4)		
Fe(2)–4B	2.20(3)	P–8Fe(1)	2.332(2)
8Fe(1)	2.498(2)	2Fe(2)	2.583(0)
2P	2.583(0)	8B	3.39(2)
4B	3.44(3)		

In a second refinement, the iron and boron positions were assumed to be fully occupied. The phosphorus position was assumed to be the subject of P/B substitution. The scattering from this position was accordingly assumed to be due to 4 $(1-r)$ phosphorus atoms and 4 r boron atoms, the fraction r being varied in the least-squares refinement. The phosphorus and boron atoms in this position were assigned fixed isotropic temperature factor values of 0.30 and 0.40 $Å^2$, respectively. After the completion of this refinement, the value for the substitution parameter r obtained was 0.09(4). The results of the last refinement are presented in Table II. The final conventional, unweighted R value for the 58 observed ($h0l$) reflexions was 0.073. A list of interatomic distances is given in Table III.

It should be observed that the unit cell dimensions for the single crystal were nearly the same as those for Sample 1 (see Tables I and II), and it may be inferred that the structural results as obtained for the single crystal can be applied to Sample 1.

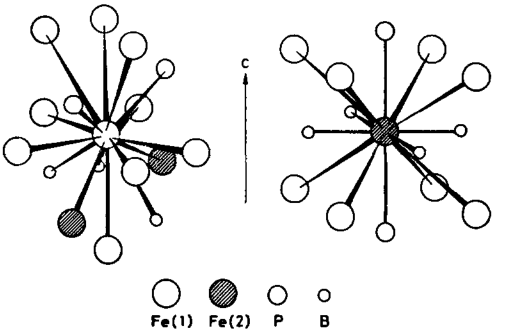

FIG. 1. The near environments of Fe(1) and Fe(2) in Fe_5PB_2.

An illustration of the near atomic environment about Fe(1) and Fe(2) in the ideally ordered Fe_5PB_2 structure is provided by Fig. 1. The Fe(1) atoms have a rather irregular environment, consisting of 11 iron atoms at distances between 2.5 and 2.9 Å, two phosphorus atoms at 2.3 Å, and three boron atoms at 2.2 Å. The Fe(2) atoms have a more regular environment. They are surrounded by eight iron atoms situated at the corners of a nearly perfect cube at a distance of 2.5 Å. Four boron atoms at a distance of 2.2 Å are situated outside four of the cube faces, and two rather remote phosphorus neighbors at 2.6 Å lie outside the remaining two cube faces.

With reference to the subsequent discussion of the Mössbauer results the following structural observations may be made. Within experimental error, the 16-fold and the fourfold iron positions contain iron atoms in the ratio of 4:1. Furthermore, the isotropic temperature factor values for the two types of iron atom are not significantly different. The refinements indicated no abnormal features for the eightfold boron position, and it seems safe to assume that this position is occupied to 100% by boron atoms. The fourfold phosphorus position thus appears to be the sole site of defects in the crystal structure.

The phase-analytical data show that the unit cell dimensions of the Fe_5PB_2 phase decrease with decreasing P/B atomic ratio. On a qualitative basis, this is compatible with either an increasing amount of phosphorus vacancies or an increasing degree of P/B substitution on the fourfold phosphorus sites. The presently available data are not sufficiently accurate for a decision to be made between the two alternatives. However, circumstantial evidence strongly favors the substitution mechanism. In transition metal phosphides, P/B substitution is very common, and in particular, substitution occurs in the three iron phosphides Fe_3P, Fe_2P, and FeP. In fact, the line Fe_3P–Fe_3B in the Fe–P–B system is characterized by an almost continuous P/B substitution. Thus, the conditions for P/B substitution are in general very favorable in the Fe–P–B system, and crystal chemical considerations give no indication that P/B substitution should be less favorable in the particular case of the Fe_5PB_2 structure. It would therefore seem very unlikely that an increase of the boron activity in the Fe_5PB_2 phase should be accompanied by an increasing amount of phosphorus vacancies rather than a successively larger P/B substitution.

For the structure of a nonstoichiometric Fe_5PB_2 crystal, the following observation may finally be made. Assume that the number of imperfections at the fourfold phosphorus positions is small, and that no more than one of the four sites in any unit cell is affected. Assume further that the crystal consists of N unit cells, and of the $4N$ phosphorus sites, the fraction r is imperfect. In one unit cell, each phosphorus site "sees" eight Fe(1) atoms and two Fe(2) atoms in its nearest environment. This means that of the $16N$ Fe(1) atoms in the crystal, $2r \cdot 16N$ atoms will have an abnormal near environment (disregarding atoms near the surface of the crystal). Similarly, the fraction $2r$ of the Fe(2) sites will have a perturbed atomic environment as compared with the remaining Fe(2) atoms. These observations are of course valid irrespective of the type of imperfection assumed, whether vacancy or replacement of a phosphorus atom by a boron atom. It may be pointed out, however, that for a nonstoichiometric crystal of the Fe_5PB_2 phase of any fixed, specific P/B atomic ratio, the number of imperfections on the fourfold phosphorus sites would be larger in the case of vacancies than in the case of P/B substitution.

4. Mössbauer Spectroscopic Studies

Representative spectra are shown in Fig. 2. The spectra obtained above the Curie temperature can be decomposed into two sets of quadrupole split lines, with an intensity ratio of about 4:1 originating from the two different crystallographic positions of iron. The deviations from the ideal ratio 4:1 in the Mössbauer spectra are clearly due to the saturation effects arising from the finite absorber thickness. The effective thickness is reduced at higher temperatures, since the recoil-free fraction decreases. In the spectrum recorded at the highest temperature, 900 K, the ratio obtained was equal to 4:1 within experimental error.

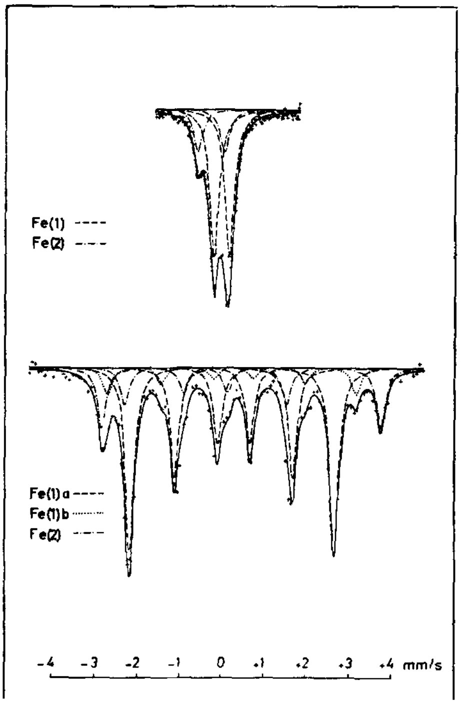

FIG. 2. Mössbauer spectra recorded at 700 K (top) and 295 K (bottom) for Sample 2 (Fe_5PB_2 (5 mg/cm^2)).

The spectra recorded below the Curie point can not be interpreted in terms of only two sets of six lines (Fig. 2). A satisfactory fit was obtained, however, by introducing an additional set. The experimental results are summarized in Table IV. In this table the quadrupole splitting Δ is defined as $(e^2qQ/2)\cdot(1+\eta^2/3)^{1/2}$ above the Curie temperature, whereas below this temperature the expression $(e^2qQ/2)\cdot(3\cos^2\theta - 1/2)$ is used. The latter formula is an approximation derived for an axially symmetric electric field gradient (efg) and a dominating magnetic

TABLE IV

RESULTS OF THE MÖSSBAUER MEASUREMENTS ON SAMPLE 2[a]

Temperature	Fe(1)a				Fe(1)b				Fe(2)				
(K)	B	δ	Δ	I	B	δ	Δ	I	B	δ	Δ	I	Γ
80	16.5(1)	0.48(1)	−0.04(1)	69(2)	19.7(1)	0.46(1)	−0.10(3)	8(2)	22.2(1)	0.23(1)	0.87(1)	23	0.32(1)
295	14.9(1)	0.35(1)	−0.03(1)	68(2)	18.2(1)	0.34(1)	−0.05(2)	10(2)	20.3(1)	0.12(1)	0.84(2)	23	0.25(1)
500	11.5(1)	0.21(1)	−0.03(1)	70(1)	13.8(3)	0.21(1)	−0.03(1)	7(2)	15.7(1)	0.00(1)	0.69(2)	23	0.33(1)
700		0.06(1)	0.36(1)	77(2)						−0.20(1)	0.63(1)	23	0.27(1)
900		−0.10(1)	0.35(1)	79(3)						−0.33(1)	0.57(1)	21	0.29(1)

[a] B is the magnetic hyperfine field in Tesla, δ the isomer shift in mm/s relative to iron metal at room temperature, Δ the electric quadrupole splitting in mm/s (see text), Γ the FWHM in mm/s and I the relative intensity in percent.

TABLE V

ROOM TEMPERATURE MÖSSBAUER RESULTS FOR THE THREE DIFFERENT SAMPLES OF Fe_5PB_2 (B, δ Δ, Γ, AND I ARE DEFINED IN TABLE IV)

	Fe(1)a				Fe(1)b				Fe(2)				
Sample	B	δ	Δ	I	B	δ	Δ	I	B	δ	Δ	I	Γ
1	14.9(1)	0.35(1)	−0.03(1)	59(2)	18.3(1)	0.34(1)	−0.04(1)	17(2)	20.6(1)	0.11(1)	0.82(1)	24	0.37(1)
2	14.9(1)	0.35(1)	−0.03(1)	68(2)	18.2(1)	0.34(1)	−0.05(2)	10(2)	20.3(1)	0.12(1)	0.84(2)	23	0.25(1)
3	14.9(1)	0.35(1)	−0.03(1)	72(2)	18.2(1)	0.29(5)	−0.12(9)	4(2)	20.0(1)	0.12(1)	0.87(2)	24	0.38(3)

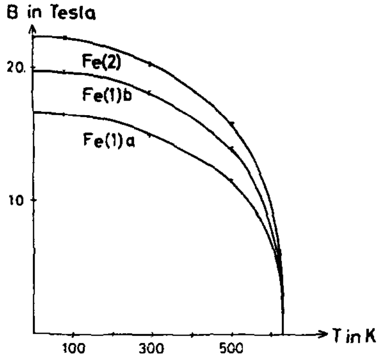

FIG. 3. Magnetic hyperfine field as a function of temperature for the different components of the Mössbauer spectra (Fe_5PB_2). $T_c = 628(11)$ K.

interaction. The strength and asymmetry of the efg is given by eq and η, respectively, eQ is the nuclear quadrupole moment and θ is the angle between the magnetic field axis and the largest component of the efg.

Using a simple point charge model and summing up the contributions from the ions situated within 40 Å from the central ion, the symmetry and orientation of the efg was calculated, assuming charges of +1 for Fe(1), +1 to +1.5 for Fe(2), −2.5 to −3 for phosphorus, and −1 to −1.5 for boron, and always fulfilling charge neutrality. For Fe(2) it was found that $\eta = 0$ and that the angle between the c axis and the efg-axis was 0° in all cases, whereas the corresponding values for Fe(1) were 0.0–0.6 and 52–55°, respectively. Admittedly, our method for estimating the efg parameters involves very drastic approximations, and any conclusions drawn from the results must necessarily be very limited. Our calculations indicate that the expressions for Δ are valid for Fe(2), while for Fe(1) with $\eta \neq 0$ the low temperature approximation for Δ might be doubtful. As will be discussed later, however, no serious errors are introduced in the present case. The temperature variation of the hyperfine parameters are shown in Figs. 3–5.

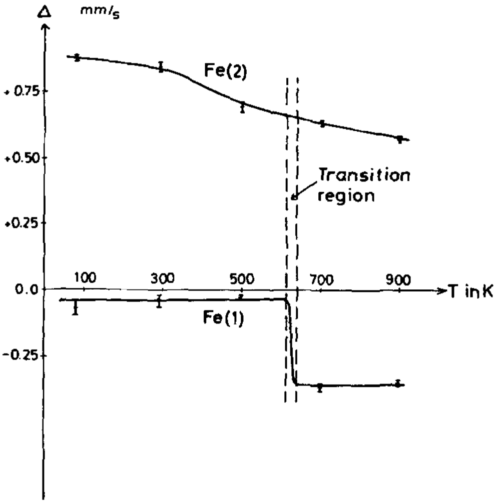

FIG. 4. The electric quadrupole splitting as a function of temperature.

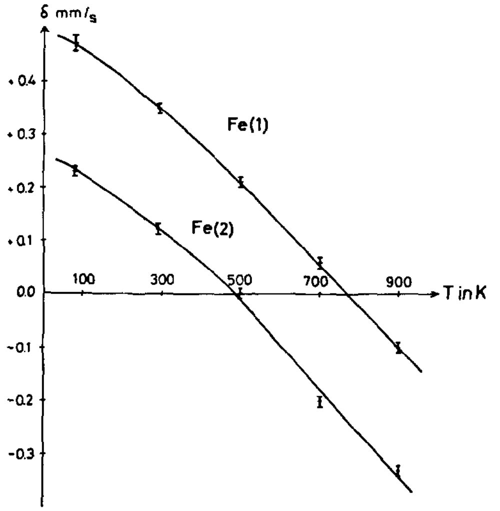

FIG. 5. The isomer shift as a function of temperature.

5. Discussion

As mentioned previously in the discussion of the crystal structure of Fe_5PB_2, a fraction of the iron atoms in nonstoichiometric Fe_5PB_2 has a perturbed near environment. This fraction becomes larger with increasing B/P atomic ratio. It is tempting to assume that the third component in the Mössbauer spectra is due to the iron atoms with a perturbed environment. This is supported by the fact that the intensity of the third component decreases successively on passing from Sample 1 to 3 (Table V), while the B/P atomic ratio decreases in the same sequence.

The isomer shifts and electric quadrupole splittings (Table IV) are closely the same for the third component and the main component. Since the latter is clearly due to Fe(1), it seems reasonable to attribute the third component to the perturbed Fe(1) atoms. This component is denoted Fe(1)*b* in the following, while the main component is denoted Fe(1)*a*. Vacancies or substitution on the phosphorus positions should produce much smaller effects for Fe(2) than for Fe(1), since the Fe(2)–P contacts are much more remote (2.58 Å) than the Fe(1)–P contacts (2.33 Å). Since there were no indications in the spectra of a fourth component, it may be assumed that the component assigned to Fe(2) is composed of contributions from all Fe(2) atoms irrespective of their environment.

In order to make a more quantitative estimation of the number of iron atoms with a perturbed environment, the Mössbauer data have to be corrected for the effects of finite absorber thickness. This correction would normally be very difficult to perform, but in the present case a simplified procedure can be used. In the spectrum of Sample 1, the peak absorptions corresponding to the maximum positive velocities for Fe(1)*b* and Fe(2) are closely the same. The intensities derived may therefore be assumed to be almost equally affected by the absorber thickness. The relative intensity for Fe(2) should ideally be 20% while the experimental value is 24%. Applying the scale factor 20/24 to the experimental value of 17% for Fe(1)*b* gives 14%. This would correspond to 18% of the total number of Fe(1) atoms, and the corresponding value for the factor r as defined in Section 3 is therefore 0.09 with an estimated error of ±0.01. This value is in good agreement with that obtained from the crystal structure refinement under the assumption of P/B substitution.

In boron-substituted Fe_3P, the magnetic hyperfine fields increase with increasing boron substitution. This may be compared with the situation in nonstoichiometric Fe_5PB_2, where the magnetic hyperfine field for Fe(1)*b* considerably exceeds that for Fe(1)*a*. By analogy it may be inferred that P/B substitution also occurs in the Fe_5PB_2 structure. The fact that the electric quadrupole interactions are equally large for Fe(1)*a* and Fe(1)*b*, may be taken as further support for this assumption. However, it is very difficult to predict the influence of phosphorus vacancies as compared with P/B substitution, and the boron atoms may well behave magnetically inactive as in the case of Fe_2B (*5*).

The smooth variation of Δ for Fe(2) on passing the Curie temperature indicates that $1/2\ (3\cos^2\theta - 1) = 1$ giving $\theta \approx 0°$. This would mean that the Fe(2) spins are parallel to the c axis, provided that the results of our efg calculations are valid. Assuming that the strength of the electric quadrupole interaction for Fe(1) is unchanged on passing the Curie point we obtain $\theta = 55(4)°$. This is the same angle as obtained from the efg calculations if we assume that also the Fe(1) spins are directed along the c axis. We therefore propose that Fe_5PB_2 is a simple ferromagnet with the c axis as the easy magnetization direction.

As a check of the applicability of the approximate formula used for Δ for Fe(1) in the present case we have diagonalized the full hyperfine hamiltonian using η and θ values around 0.3 and 54°, respectively. It turns out that the formula used is a very good approximation and that only minute changes in line position result from the use of the full hamiltonian.

As regards the isomer shifts, the temperature variation is entirely compatible with the second order Doppler shifts.

6. Conclusions

The results from our studies of Fe_5PB_2 can be summarized as follows.

For ideal stoichiometric Fe_5PB_2 the Mössbauer spectra are composed of two components, one from each of the two crystallographically nonequivalent types of iron atom Fe(1) and Fe(2). A closer analysis of the spectra indicates that Fe_5PB_2 is a simple ferromagnet with the tetragonal axis as the direction of easy magnetization. From the magnetic moment of 1.73 μ_B per iron atom the individual moments can be calculated from the values of the magnetic hyperfine fields and are obtained as 1.62 μ_B (Fe(1)) and 2.16 μ_B (Fe(2)).

For nonstoichiometric Fe_5PB_2 crystallographic evidence indicates that the phosphorus positions are the sole sites of defects in the structure. The deviations from the ideal composition are most likely associated with P/B substitution at the phosphorus positions. The Mössbauer spectra contain a third component, the intensity of which increases with increasing B/P atomic ratio. This component is ascribed to Fe(1) atoms, for which one of the surrounding phosphorus atoms has been replaced by a boron atom.

7. Acknowledgments

This work was financially supported by the *Swedish Natural Science Research Council* and the Carl Trygger Foundation for scientific research.

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