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Magnetic Structure of Iron Monophosphide†

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Neutron-diffraction measurements have shown that FeP is magnetically ordered below 125 °K. The magnetic structure is a "double helix," propagating along the *c* axis of the *Pnma* crystal structure with a period of 29.2 Å. The magnetic structure allows two different sites for the iron atoms, with magnetic moments $\mu_1 = 0.46\mu_B$, $\mu_2 = 0.37\mu_B$. The form factor for iron is considerably more expanded than the calculated 3*d* free-atom form factor.

I. INTRODUCTION

The magnetic properties of iron phosphide have been studied by several authors. The reported properties were often in conflict because of the inability to prepare a well-defined homogeneous phase of FeP. Chiba[1] first reported FeP to be paramagnetic with typical Curie-Weiss behavior in the temperature range 290–900 °K. Meyer and Cadeville,[2] in a later study, indicated that FeP was ferromagnetic with a Curie point of 215 °K. Above the Curie point, FeP followed a Curie-Weiss behavior, but with constants differing considerably from those reported by Chiba. In a recent study of transition-metal monophosphides, Stein and Wamsley[3] observed essentially temperature-independent paramagnetic behavior for FeP. A similar result was obtained by Roger and Fruchart.[4,5] However, Bailey and Duncan[6] reported that at 90 °K a broad asymmetric Mössbauer absorption line was visible.

Recent magnetic measurements,[7] performed on very pure samples, indicated that the susceptibility of the compound is rather low, but not temperature independent; it shows an anomalous behavior—suggestive of magnetic transition—around 120 °K (Fig. 1). The present neutron-diffraction investigation was undertaken in order to determine whether magnetic transition occurs and to establish the magnetic structure.

The crystal structure of FeP is well known[8]; it is orthorhombic, of MnP type, with space group *Pnma*. The reported cell dimensions are, at room temperature, $a = 5.187$ Å, $b = 3.093$ Å, $c = 5.793$ Å. Both Fe and P occupy the *c* positions of the *Pnma* space group:

$$x, \tfrac{1}{4}, z \;[1]; \qquad \tfrac{1}{2}+x, \tfrac{1}{4}, \tfrac{1}{2}-z \;[2]; \qquad \tfrac{1}{2}-x, \tfrac{3}{4}, \tfrac{1}{2}+z \;[3]; \qquad -x, \tfrac{3}{4}, -z \;[4]; \tag{1}$$

with reported parameters

$$\begin{aligned} &\text{Fe: } x = 0.005, \quad z = 0.200, \\ &\text{P: } x = 0.190, \quad z = 0.570. \end{aligned} \tag{2}$$

The labeling of the atoms is for later convenience in the analysis of the magnetic structure.

II. EXPERIMENTAL

The neutron-diffraction measurements were made at the CP-5 reactor at ANL on a two-axis spectrometer that utilized $\lambda = 1.171$ Å neutrons. The samples used were 5-g powder, 100-mesh grain, and a single crystal with a volume of approximately 2 mm^3. Both samples were prepared at Brown University.[7]

The initial information on the system was gathered from slow powder scans at room temperature and at 78 °K. The room-temperature pattern revealed only the lines belonging to FeP; a least-square analysis over nine groups of peaks gave essentially the same atomic parameters reported in the literature. At 78 °K the agreement between the observed and the calculated intensities was only slightly worse than at room temperature; however, around the (101) nuclear line appeared two peaks, so weak that several runs were necessary to determine them

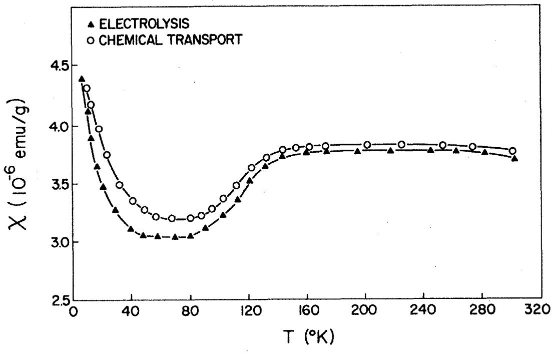

FIG. 1. Temperature dependence of the susceptibility of FeP (from Bellavance *et al.*, Ref. 7).

TABLE I. Observed and calculated intensities of the magnetic satellites of FeP at 4.2 °K.

Index	$(\sin\theta)/\lambda$	Experiment	Model 1	Model 2
000^+	0.017	3487 ± 100	3410	3666
001^-	0.069	0 ± 8	0	0
100^-	0.098	0 ± 24	7	6
100^+	0.098	0 ± 24	7	6
001^+	0.103	0 ± 6	0	0
101^-	0.119	6823 ± 60	6936	6754
101^+	0.141	4743 ± 60	4736	4821
002^-	0.155	1529 ± 90	1219	1393
200^+	0.193	115 ± 24	88	105
201^-	0.205	0 ± 18	0	0
102^+	0.213	0 ± 18	3	2
003^-	0.242	0 ± 30	0	0
202^-	0.248	454 ± 70	325	395
103^-	0.260	1282 ± 40	1171	1230
202^+	0.270	856 ± 70	845	890
003^+	0.276	0 ± 24	0	0
103^+	0.292	338 ± 30	282	344
301^-	0.297	878 ± 50	830	888
301^+	0.307	602 ± 50	615	674
004^-	0.328	998 ± 30	904	980
004^+	0.362	841 ± 90	786	853
303^-	0.376	249 ± 30	279	271
204^-	0.381	396 ± 26	474	478
303^+	0.400	127 ± 30	77	83
204^+	0.410	513 ± 170	477	436
402^-	0.416	0 ± 30	51	5
402^+	0.430	60 ± 140	145	123

properly. A quick check showed that the "spurious" peaks were not easily indexable in terms of the chemical cell of FeP, nor were they assignable to the most obvious magnetic impurities. They were instead consistent with a magnetic modulation along the *c* axis of FeP, with a period of 28.7 Å, and then they could be labeled as satellites (101^-), (101^+).

In order to check the existence and to determine the nature of the magnetic structure, single-crystal data were taken in the [010] zone at room temperature, 78, 32, 15, and 4.2 °K. At room temperature, the crystal was seen to be not entirely single, but to consist of one main crystal and a small twin crystal, whose scattering effects were accounted for. At 78 °K and below, magnetic satellites appeared at the predicted points of the reciprocal space. No satellites, other than the ones predicted by a simple modulation, were observable.

In Table I a compendium of the integrated intensities of the satellites is presented, as observed at 4.2 °K. All satellites are at $(\sin\theta)/\lambda < 0.45$ Å^{-1}, a region for which the peaks have reasonable intensities. The errors indicated are, for most reflections, experimental errors as obtained by taking several rocking curves for each reflection in different quadrants of the [010] zone; however, for the weakest reflections the errors are statistical, since the different runs had to be summed up in order to obtain recognizable peaks.

While the intensity of the nuclear peaks was rather affected by extinction and multiple scattering, no evidence of these effects was found in the magnetic satellites. The absence of extinction seems reasonable, since the magnetic cross section is quite small in comparison with the nuclear cross section; double scattering could be considerably more important because on the surface of the Ewald's sphere, in the condition of reflection of one satellite, another satellite or a nuclear reflection could occur. However, in the chosen setting of the crystal the coupled reflections are generally too weak to affect the intensity of the single-scattering processes.

The intensities of Table I were used directly to obtain the magnetic structure; the absolute size of the magnetic moments was instead deduced from the powder measurements.

Smaller sets of reflections were obtained at different temperatures and were used only to check whether or not the main features of the magnetic ordering changed with temperature.

III. ANALYSIS OF MAGNETIC STRUCTURE

Table I shows that pairs of satellites attributed to the same nuclear line have markedly different intensity. Such a behavior has been already observed in the isostructural MnP (below 50 °K)[9,10] and CrAs,[11] and it has been shown to be due to a "double helix" magnetic structure; hence, it seems natural to deal with FeP in a similar way.

The essential formulas used will be recalled here. The scattered intensity due to a periodic magnetic structure is proportional to [12,13]

$$|\hat{k}\times\{\hat{k}\times\textstyle\sum_L\sum_j f_j\vec{\mu}_j^L\exp[2\pi i\vec{k}\cdot(\vec{R}_L+\vec{r}_j)]\}|^2, \qquad (3)$$

where $\vec{k}$ is the scattering vector (and $\hat{k}$ the unit vector in the same direction); $\vec{R}_L$ is the vector position of the *L* chemical cell; $\vec{r}$, the position of the magnetic atom *j* in the cell, with magnetic moment $\vec{\mu}_j^L$ and form factor f_j.

For a magnetic structure characterized by a single modulation vector $\vec{\tau}$, the Fourier transformation of the spin vector gives

$$\vec{\mu}_j^L=\vec{\mu}_j^\tau e^{2\pi i\vec{\tau}\cdot(\vec{R}_L+\vec{r}_j)}+\vec{\mu}_j^{-\tau}e^{-2\pi i\vec{\tau}\cdot(\vec{R}_L+\vec{r}_j)}, \qquad (4)$$

where $\vec{\mu}_j^{-\tau}=\vec{\mu}_j^{\tau *}$. Expression (3) now becomes

$$|\hat{k}\times\{\hat{k}\times[(\textstyle\sum_j f_j\vec{\mu}_j^\tau e^{2\pi i(\vec{k}+\vec{\tau})\cdot\vec{r}_j})(\sum_L e^{2\pi i(\vec{k}+\vec{\tau})\cdot\vec{R}_L})$$

$$+(\textstyle\sum_j f_j\vec{\mu}_j^{-\tau}e^{2\pi i(\vec{k}-\vec{\tau})\cdot\vec{r}_j})(\sum_L e^{2\pi i(\vec{k}-\vec{\tau})\cdot\vec{R}_L})]\}|^2. \qquad (5)$$

Expression (5) shows that the magnetic structure gives two sets of peaks: one for $\vec{k}+\vec{\tau}=\vec{B}_{hkl}$ (satellites "minus") and the other for $\vec{k}-\vec{\tau}=\vec{B}_{hkl}$ (satellites "plus"), where $\vec{B}_{hkl}$ is a reciprocal-lattice vector. From the measurement of magnetic intensities it is possible to determine $\vec{\mu}_j^\tau$, or the "basis" of the modulated structure. If the modulation has spiral character, one can write

$$\vec{\mu}_j^\tau = \mu_j(\vec{i} - i\vec{j})e^{2\pi i \delta_j} , \tag{6}$$

where $\vec{i}$, $\vec{j}$ are unitary vectors defining fixed orthogonal coordinates.

A. Model 1

In applying (3)–(6) to the specific case of FeP, a few simplifying hypotheses were made. It is assumed that only Fe has a magnetic moment μ. Its size is taken the same for the four crystallographic equivalent atoms of the chemical cell. The form factor is also assumed to be the same for all Fe atoms, and a smooth function of $|k|$ in the region considered $[(\sin\theta)/\lambda < 0.45\ \text{A}^{-1}]$. The modulation is assumed to have a spiral character. The structure factor for the magnetic peaks in the [010] zone can then be written (leaving out the form factor)

$$\begin{aligned} F_{h0l}^{\pm} = \mu \big(& \exp[2\pi i(xh + zl \mp \delta_1)] \\ & + \exp\{2\pi i[(\tfrac{1}{2}+x)h + (\tfrac{1}{2}-z)l \mp \delta_2]\} \\ & + \exp\{2\pi i[(\tfrac{1}{2}-x)h + (\tfrac{1}{2}+z)l \mp \delta_3]\} \\ & + \exp[2\pi i(-xh - zl \mp \delta_4)]\big). \end{aligned} \tag{7}$$

If all δ_i were the same, the spin structure could transform under the symmetry operations of the crystallographic space group *Pnma*, but then $F_{h0l}^{+} = F_{h0l}^{-}$ in contradiction to the experimental results. The δ_i's can be taken equal in pairs; three combinations are then possible. If $\delta_1 = \delta_2$, or if $\delta_1 = \delta_4$, it is easily seen that $F^{+}_{h0l} \neq F^{-}_{h0l}$ but $F^{\pm}_{h0l} = F^{\mp}_{h0l}$; by measuring the intensities of the satellites in different quandrants of the [010] zone, these combinations were ruled out. If $\delta_1 = \delta_3$, (7) can be rewritten

$$\begin{aligned} F_{h0l}^{\pm} = {} & \mu_{\mathrm{F}}\{\cos 2\pi(xh+zl) + \cos 2\pi[(\tfrac{1}{2}+x)h + (\tfrac{1}{2}-z)l]\} \\ & \pm \mu_{\mathrm{AF}}\{\sin 2\pi(xh+zl) - \sin 2\pi[(\tfrac{1}{2}+x)h + (\tfrac{1}{2}-z)l]\}. \end{aligned} \tag{8}$$

The moments on Fe are split into a "ferromagnetic" component and an "antiferromagnetic" component normal to it. We then tried to fit the experimental data with (8) and with a smooth form factor. The latter was chosen, rather arbitrarily, as the sum of three Gaussians containing three adjustable parameters. It was found that the best fit is obtained when the magnetic moments lie in the plane normal to the c axis, and their components assume the values $\mu_{\mathrm{AF}} = 0.41\mu_B$, $\mu_{\mathrm{F}} = -0.08\mu_B$, giving the basis of the spiral illustrated in Fig. 2(a). The absolute size of the magnetic moments is deduced from the powder data, and it is accurate within 10%.

The best form factor obtained by least-square fitting has the form

$$f\left(\frac{\sin\theta}{\lambda}\right) = \frac{1}{2.234}\left\{\exp\left[-13\left(\frac{\sin\theta}{\lambda}\right)^2\right] + \exp\left[-4.6\left(\frac{\sin\theta}{\lambda}\right)^2\right] + 0.234\right\} , \tag{9}$$

and it is represented in Fig. 3(a) together with the values deduced from the experimental intensities.

B. Model 2

Figure 3(a) shows that the model chosen fits the experimental data fairly well but that there are discrepancies that cannot be attributed easily to errors in the measurements. A refinement of the model was then attempted by reviewing the hypotheses made in the preceding paragraph. Model 1 contains a possible contradiction. The Fe atoms are assumed to have the same magnetic moment since they are crystallographically equivalent (they occupy the c position of the *Pnma* space group); but the structure factor used in model 1 is that of a spin structure not transforming under the symmetry

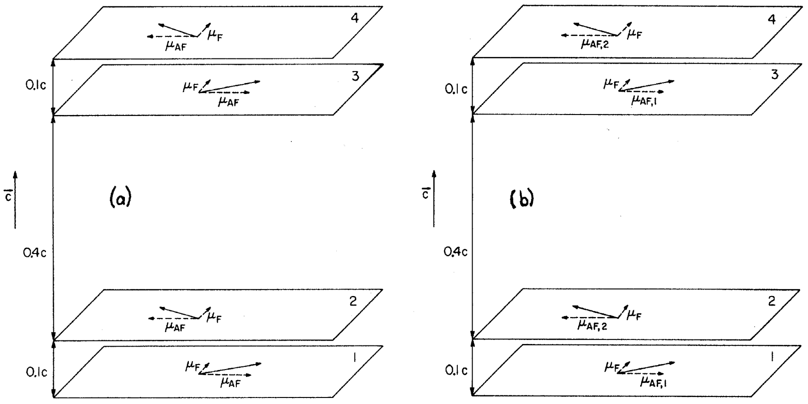

FIG. 2. Basis of the spiral structure: The planes indicate layers of atoms with the same phase. c is the dimension of the chemical cell along the c axis. The actual magnetic structure is obtained by rotating the moments on each layer of an angle proportional to the distance from the bottom layer. (a) Basis for model 1: all magnetic moments are equal. (b) Basis for model 2: two sets of magnetic moments.

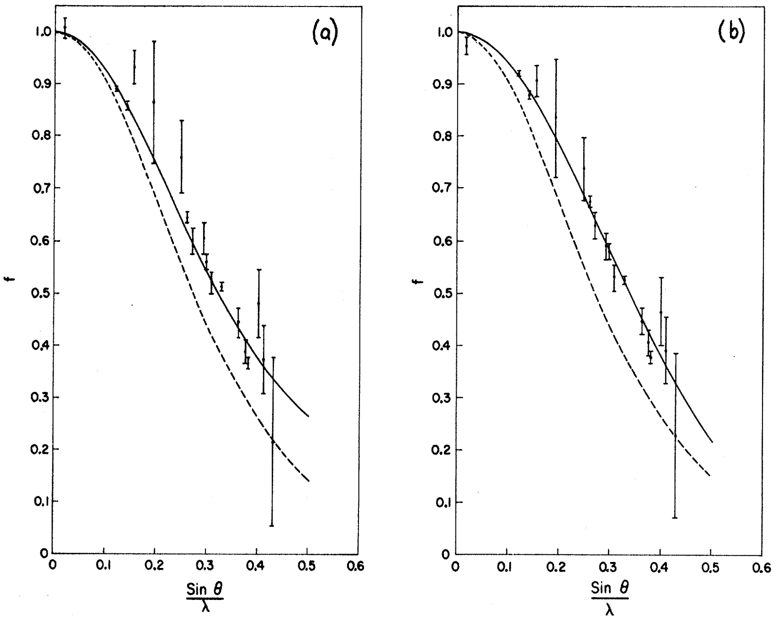

FIG. 3. Form factor as obtained from the experimental data: (a) for model 1, (b) for model 2. Solid lines indicate the empirical form factors used; dotted lines, the Freeman-Watson 3*d* form factor for free iron atom.

operations of the *Pnma* space group. Bertaut[14] has shown that, for a similar magnetic configuration, the spin structure transforms under the symmetry operations of the $Pnm2_1$ space group, according to which the iron atoms are no longer equivalent but split into two groups 1, 3; 2, 4. The two groups of atoms do not have necessarily the same magnetic moment.

In model 2 it was assumed arbitrarily that the difference in magnetic moments is affecting only the larger component μ_{AF} and that the form factor remains the same for all Fe atoms. Then the structure factor becomes

$$\begin{aligned} F^{\pm}_{h0l} = {} & \mu_F\{\cos 2\pi(xh+zl) + \cos 2\pi[(\tfrac{1}{2}+x)h + (\tfrac{1}{2}-z)l]\} \\ & \pm \mu_{AF}\{\sin 2\pi(xh+zl) - \sin 2\pi[(\tfrac{1}{2}+x)h + (\tfrac{1}{2}-z)l]\} \\ & \pm \tfrac{1}{2}\, i\, \Delta\mu\, \{\cos 2\pi(xh+zl) + \cos 2\pi[(\tfrac{1}{2}+x)h + (\tfrac{1}{2}-z)l]\}, \end{aligned} \tag{10}$$

where $\Delta\mu = |\mu_{AF1,3} - \mu_{AF2,4}|$. Since the third component of (10) is imaginary, it is not possible by neutron diffraction to assign the higher moment to atoms [1], [3] or to atoms [2], [4]. Proceeding in the same way as for model 1, it was found that

$$\mu_{AF} = 0.41\mu_B, \quad \mu_F = -0.07\mu_B, \quad \tfrac{1}{2}\Delta\mu = 0.05\mu_B .$$

These moments give the basis of the spiral illustrated at Fig. 2(b) or the alternate one, obtained by switching the size of the "antiferromagnetic" component of atoms 1, 3 with the one of atoms 2, 4. The absolute size of the magnetic moments is, as for model 1, accurate within 10%.

The form factor chosen this time had a simpler analytical form; it was merely a Gaussian, so that only one parameter had to be refined. The best fit gave

$$f\left(\frac{\sin\theta}{\lambda}\right) = \exp\left[-6.07\left(\frac{\sin\theta}{\lambda}\right)^2\right], \tag{11}$$

plotted in Fig. 3(b), together with the values deduced from the experimental intensities. The improvement obtained over model 1 is quite visible; it was felt that further refinement would not be of physical significance.

It has to be pointed out that model 2 constitutes an improvement over model 1 only because the experimental data are brought in closer agreement with a smooth form factor. Model 2 was suggested by a close analysis of the inconsistencies of model 1, independently from any consideration on the symmetry of the system. Before finding it empirically, many attempts were made to reach a better fit of the experimental data with a model that does not ask for two different magnetic moments on the Fe sites.

It is perhaps worthy to reemphasize that the possible corrections to be brought to the experimental intensities were rather carefully checked: The extinction on the highest magnetic peak was estimated from the nuclear intensities to be not larger than 2%, and the second-order satellites, typical indicators of double-scattering processes in the spiral structures, were found to be absent. Even dropping one or two reflections from the refinement program did not alter significantly the fit or the values of the parameters.

Several variations of model 1 were tried. Thus, to the form factor was assigned a different analytical expression; magnetic moments were allowed on the phosphorus sites; the atomic parameters were varied in a reasonable range, and the projection of the spiral onto the (001) plane was considered an ellipse rather than a circle. All these attempts were unsuccessful.

IV. FORM FACTOR

The FeP magnetic structure seems particularly suitable for obtaining an accurate form factor for low *k* values, since many experimental points fall in that region. In the early stages of the experiment it was hoped that FeP, having good metallic properties, might show some *s* electron polarization as a deviation of the experimental points at very low *k* from the free-atom form factor. For all the other points we expected to have a good fit with the form factor calculated by Freeman and Watson[15] for the 3*d* spins in the free atom, which is usually in close agreement with the experiments on metallic iron compounds. The set of experimental data [with the exception of (000^+)] was analyzed, in both models 1 and 2, assuming the Freeman-Watson form factor; it was found that the fit was poor and the deviations were systematic. We then decided to allow the form factor to vary in the way previously discussed.

The normalized F-W form factor is plotted for comparison with the empirical one and with the experimental data in Figs. 3(a) and 3(b). It is apparent that iron in FeP has a more expanded form factor than normal metallic iron.[16] In order to understand the reasons for such anomalous behavior, the relative weights of the orbital moment and the spin should be known. An attempt was made to determine the gyromagnetic ratio with electron paramagnetic resonance,[17] but no resonance was found at room temperature.

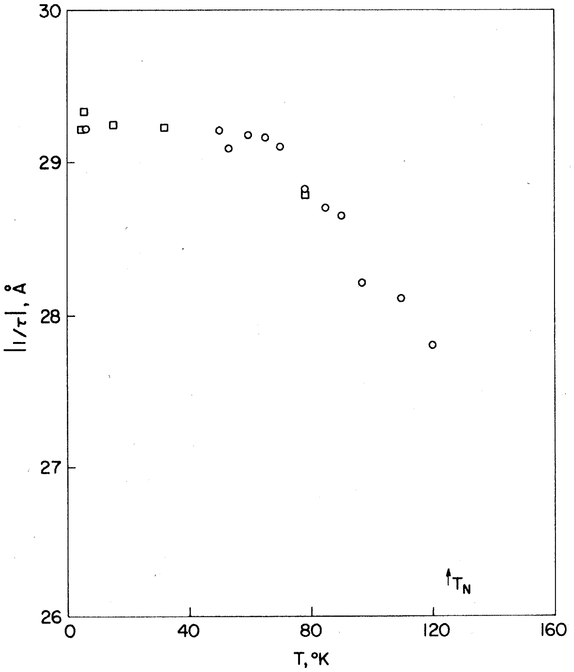

FIG. 4. Temperature dependence of the period of the spiral. □, obtained from the positions of sets of reflections ○, obtained from the positions of the (000^+), $(101)^-$, (101^+) satellites only.

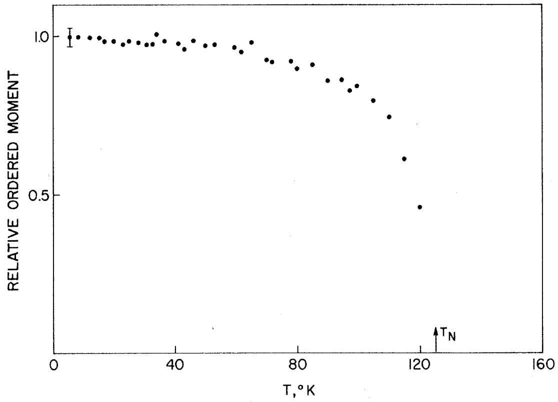

FIG. 5. Temperature dependence of the ordered magnetic moment, as obtained from the (000^+) reflection.

Even if the *g* ratio were known, the data do not extend far enough in the *k* space to obtain a direct determination of the spin density from Fourier transformation; it would be possible only to compare the data with the form factors calculated for a free atom[15] or a band structure.[18] If the *g* factor were found to be not very different from 2, it would be tempting to correlate the low moment on iron with the expanded form factor; iron in FeP would behave more like nickel, or it would show that the top of the 3*d* band is more contracted.[19]

V. TEMPERATURE BEHAVIOR

The magnetic susceptibility of FeP (Fig. 1) shows a drastic change of slope between 20 and 40 °K. In the same temperature region, anomalies in the resistivity and in the Hall coefficient[7] were reported.

In order to determine if the anomalies corresponded to a change of the magnetic structure or of the form factor, intensity measurements were taken on sets of reflections (each set consisting in average of eight visible reflections) at 5.5, 14, 32, and 78 °K. The intensities of the three satellites (000^+), (101^-), (101^+) were also taken at more closely spaced temperatures, up to 125 °K.

The sets of eight reflections at the four temperatures mentioned above were not sufficient to allow the determination of all the physical parameters to the accuracy of the results at 4.2 °K. The ratio between the two components of the moments μ_{AF} and μ_F remained approximately constant, the max-

TABLE II. Magnetic properties of compounds with *Pnma* crystal structure, and "double helix" magnetic structure.

Compound	T_N(°K)	$1/\tau$ [a]	μ	$\varphi_{1,2}$ [b]	Properties at
CrAs	280	~ 2.8	$2\mu_B$	$-89.4°$	96 °K (Ref. 11)
MnP	50[c]	~ 9	$1.3\mu_B$	$+16.0°$	4.2 °K (Refs. 9, 10)
FeP	125	~ 5	$0.41\mu_B$	$+168.8°$	4.2 °K (Present work)

[a] In units of the chemical cell along the *c* axis.

[b] Angle between atom 1 and 2 in the basis of the spiral.

[c] Temperature at which there is an antiferromagnetic-ferromagnetic transition.

imum deviation being of the order of 10%. The parametric coefficient in the form factor, expressed by (11), also varied within 10%. The data were not sufficient to refine $\Delta\mu$. Therefore, if there is a variation of the magnetic structure or of the form factor with the temperature, it is rather subtle. This was confirmed by the fact that the behavior of the intensities as a function of the temperature is practically the same for the three satellites (000^+), (101^-), (101^+). It was therefore assumed that both the magnetic structure and the form factor remain constant with temperature, and the measurements were used to determine the variation of the period of the spiral and the variation of the ordered moments with the temperature.

The period of the spiral (Fig. 4) has a temperature behavior similar to that found in the rare earths.[20] No anomalies were found for the lattice parameters *a* and *c*, which increase smoothly with the temperature or for the atomic parameters, which remain essentially constant.

In Fig. 5 is reported the temperature behavior of the site magnetization as obtained from the (000^+) satellite. The data are not accurate enough to establish whether, at low temperatures, the magnetization varies with T^2 or with a different law. From this curve, and the ones obtained from the intensities of the (101^-), (101^+) satellites, a Néel temperature of (125 ± 1)°K was found.

VI. CONCLUSIONS

Iron phosphide has a magnetic structure of the "double-helix" kind. Other compounds, crystallizing in the *Pnma* space group, were previously found to have the same magnetic structure: MnP[9,10] and CrAs.[11] A considerable amount of theoretical work has been done to explain this kind of magnetic structure; Takeuchi and Motizuki[21] explain the stability of the double-helix structure in MnP by assuming only isotropic exchange interactions and seven different exchange constants. Bertaut[14] points out that, if an antisymmetric coupling is introduced, the stability of the double helix can be explained in terms of only three exchange constants. The theoretical effort up to now has concentrated on the magnetic structure of MnP; Table II presents a compendium of the experimental properties found in similar compounds. It can be noticed from the table that the period of the spiral varies greatly from compound to compound, and does not approach a "magic" value as for the rare earths[20]; this fact suggests that the magnetic interactions are here considerably more complex. The magnetic moments decrease in the series, from Cr to Fe. On CoP only magnetic measurements have been made[3]; these show that the susceptibility is approximately one-fourth of the one found for FeP and changes only slightly with temperature.

The present experiment shows that better consistency is reached if the magnetic moments on iron are assigned on the basis of the magnetic symmetry, rather than on the apparent crystal symmetry; these are found to be $\mu_1 = 0.46 \pm 0.04$, $\mu_2 = 0.37 \pm 0.04$. The form factor of Fe in FeP appears to be considerably more expanded than the "normal" form factor for metallic iron. In order to explain such findings, a considerable amount of experimental work remains to be done.

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PHYSICAL REVIEW B VOLUME 3, NUMBER 9 1 MAY 1971

Quasiclassical Spin Dynamics for the Heisenberg Model*

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The Wigner method is employed to develop explicit relationships among quantum-mechanical and classical equations of motion and quantum-mechanical and classical pair-correlation functions of spin operators. In this method, quantum corrections to the classical theory can be accurately estimated. The formalism is applied to a spin-$\frac{1}{2}$ Heisenberg model at high temperatures. The most attractive feature of this method is that many of the results are intuitively satisfying. Finally, we make a connection between our results and the classical calculations made by several other authors.

I. INTRODUCTION

The classical theory of spin dynamics, in which the quantum-mechanical spin operators are replaced by classical vectors of fixed length, has been investigated both analytically[1] and numerically.[2]

In particular, these authors consider the spin-spin pair-correlation function

$$\Gamma_{ii'}^{\alpha\alpha'}(t)=\frac{\mathrm{Tr}[S_{i\alpha}S_{i'\alpha'}(t)+S_{i'\alpha'}(t)S_{i\alpha}]e^{-\beta H}}{2\,\mathrm{Tr}\,e^{-\beta H}}, \quad (1)$$

where i and i' label the individual spins, α and α' label Cartesian components and, of course, $\hbar S_{i\alpha}(t)$ is the Heisenberg operator for the αth component of the spin operator for the ith spin. The "classical" approximation for the spin-j case consists of substituting vectors $j\vec{\Omega}_i$ for $\vec{S}_i$, where the $\vec{\Omega}_i$'s are unit vectors, and integrating over the $\vec{\Omega}_i$'s:

$$\Gamma_{ii'}^{\alpha\alpha'}(t)\cong j^2\int d\vec{\Omega}_1\cdots d\vec{\Omega}_N\,\Omega_{i\alpha}\,\Omega_{i'\alpha'}(t)\,e^{-\beta H_{\mathrm{cl}}}\Big/\int d\vec{\Omega}_1\cdots d\vec{\Omega}_N\,e^{-\beta H_{\mathrm{cl}}}\,. \quad (2)$$

The "classical" Hamiltonian $H_{\mathrm{cl}}(\vec{\Omega}_1\cdots\vec{\Omega}_N)$ is obtained from $H(\vec{S}_1\cdots\vec{S}_N)$ by substituting $j\vec{\Omega}_i$ for $\vec{S}_i$.

The factor $\vec{\Omega}_i(t)$ satisfies a classical equation consistent with $H_{\mathrm{cl}}(\vec{\Omega}_1\cdots\vec{\Omega}_N)$. For example, if H is given by the Heisenberg model

$$H=-\sum_{i\neq i'}J_{ii'}\vec{S}_i\cdot\vec{S}_{i'}\,, \quad (3)$$

the classical Hamiltonian is

$$H_{\mathrm{cl}}=-\sum_{i\neq i'}j^2J_{ii'}\vec{\Omega}_i\cdot\vec{\Omega}_{i'} \quad (4)$$

and the classical equation of motion is

$$\frac{d}{dt}\vec{\Omega}_i(t)=\frac{2j}{\hbar}\sum_{i'\neq i}J_{ii'}\vec{\Omega}_i(t)\times\vec{\Omega}_{i'}(t)\,. \quad (5)$$

Some authors make somewhat different substitutions using $[j(j+1)]^{1/2}\vec{\Omega}_i$ rather than $j\vec{\Omega}_i$. However, in neither case is it at all clear how closely the result approximates Eq. (1).

The use of the classical approximation simplifies the computations considerably. It even makes it possible to study spin dynamics by directly solving the equation of motion for a large (~1000) number of coupled spins.