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The magnetic properties of hexagonal Fe₂P single crystal are studied by the measurements of magnetization, susceptibility, thermal expansion and electrical resistivity along the principal crystallographic axes. It is found that the saturation magnetization per molecule and the Curie temperature are 2.94 μ_B and 208.6 K, respectively, and the anisotropy constant K_1 is 2.32×10^7 erg/cm³ at 4.2 K, which is considerably larger than the values in 3d-transition compounds. The thermal expansion and the electrical resistivity show discontinuous changes at the Curie temperature indicating that the ferromagnetic to paramagnetic transition of Fe₂P is accompanied by the first-order transition due to magnetoelastic effects. The exchange striction obtained from the measurement of thermal expansion is discussed on the basis of the theory of Bean and Rodbell.

§1. Introduction

The crystal structure of Fe₂P compound was first investigated by Rundqvist and Jelinek¹⁾ and refined recently by Carlsson *et al.*²⁾ This compound has a hexagonal structure with a space group D_{3h}³ (P6̄2m), in which P atoms form a channel lined along the direction of the *c* axis and there are two non-equivalent Fe-atom sites. One of the two, Fe_I, is surrounded by four P-atoms which form a nearly cubic tetrahedron and the other is Fe_{II} surrounded by five P-atoms which form a pyramid as shown in Fig. 1(a). The Fe₂P structure is built up from

a hexagonal packing of these channel pairs as shown in Fig. 1(b).

Magnetic studies of Fe₂P compound have been done by many investigators, but there are considerable disagreements in the magnetic properties. The ferromagnetic Curie temperature has been obtained as 306 K by Chiba,³⁾ 266 K by Meyer and Cadeville,⁴⁾ 266 K by Fruchart *et al.*,⁵⁾ 226 K by Bellavance *et al.*⁶⁾ and 214.5 K by Wäppling *et al.*⁷⁾ The value of magnetic moment per formula unit has been measured as 2.65 μ_B by Meyer and Cadeville,⁴⁾ 2.70 μ_B by Bellavance *et al.*⁶⁾ and 2.92 μ_B by Lundgren *et al.*⁸⁾ There are also some differences in the hyperfine field obtained by the Mössbauer effect experiment. The hyperfine fields at Fe_I and Fe_{II} at 77 K were reported, respectively, as 117 and 175 kOe by Sato *et al.*,⁹⁾ 110 and 140 kOe by Bailey and Duncan¹⁰⁾ and 109 and 172 kOe by Wäppling *et al.*¹¹⁾ These disagreements may suggest that the slight differences of impurities and stoichiometry have serious effects on the magnetic properties as described by Meyer and Cadeville.⁴⁾ In the present paper, the measurements of magnetization, paramagnetic susceptibility, thermal expansion and electrical resistivity have been carried out on the single crystals prepared carefully to know intrinsic magnetic properties of Fe₂P compound.

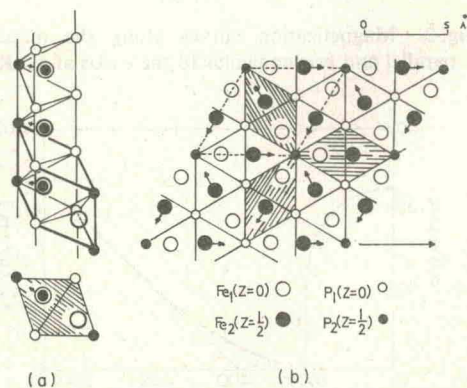


Fig. 1. Crystal structure of Fe₂P. (a) Relationship of Pyramidal-site and tetrahedral-site atoms. (b) Arrangement of rhombo-hedra subcells.

§2. Sample Preparation and Experimental Procedure

The compound was prepared by solid-vapor reaction. The mixture of the stoichiometric proportion of iron, 99.99% in purity of a powder form, and phosphorous, 99.999% in purity, was sealed in an evacuated quartz tube and then heated slowly up to 900°C for three days in a furnace and maintained at 900°C for two weeks and cooled in the furnace. The product was ground into powder, again sealed in a quartz tube with an argon atmosphere, melted at 1450°C for about 30 minutes and rapidly cooled in a water. The compound thus prepared was checked by X-ray diffraction to ascertain a single phase, and the deviations of stoichiometry in the ingot was not found with the test of the magnetic measurement of all the parts of the ingot. The single crystal was grown in an evacuated quartz tube by the thermal annealing of this ingot just below the eutectic point. From this crystal, a sphere-shaped specimen of 3 mm in diameter was prepared by the two-pipe lapidary method for the magnetic measurements. A cube specimen of $7 \times 7 \times 7$ mm³ with parallel surface to the *ab*, *bc* and *ac* planes was cut out for the measurements of thermal expansion. For the measurements of the electrical resistivity, the rectangular parallelepiped specimens of $1 \times 1 \times 7$ mm³ were cut out having the *c*- or *b*-axis direction along the longitudinal direction of the specimen. The magnetization of the single crystal was measured within an error of 1% by using a Foner-type vibrating-sample magnetometer in the applied field up to 50 kOe in the temperatures from 4.2 to 250 K. The paramagnetic susceptibility was measured within an error of 1% by using an automatic magnetic balance in the temperatures from room temperature to 700 K. The electrical resistance was measured by a standard four-probe method in the range from 77 K to 650 K with current reversal. As the current leads and potential probes the manganin wires of 0.2 mm in diameter were spot-welded on the specimen. The cross area of the specimen and the distance between the potential probes were measured with an accuracy of ± 0.01 mm. The measurements of thermal expansion were made by a dilatometer with an unbonded strain-gauge with an accuracy of $\pm 5 \times 10^{-5}$

mm.¹²⁾

§3. Results

Figure 2 shows the magnetization curves along the directions parallel and perpendicular to the *c* axis at 4.2 K. It is seen that the easy axis of magnetization is the *c* axis and the hexagonal anisotropy is very large. No magnetic anisotropy in the basal plane could be observed. The saturation magnetic moment is $2.94 \mu_B$ per formula unit which is in good agreement with that obtained by Lundgren *et al.*⁸⁾ This value is nearly equal to $3.0 \mu_B$ which is the spin only value in the formal valences predicted by Goodenough.¹³⁾

Figure 3 shows the temperature dependence of saturation magnetic moment σ_g and inverse susceptibility χ_g^{-1} . The temperature dependence of σ_g displays in accord with the Brillouin function for $j = \frac{3}{2}$ rather than for $j = \frac{1}{2}$ except for in the vicinity of the Curie temperature. The rapid decrease of moment in the vicinity of the Curie temperature is attributed to the fact that the ferromagnetic to paramagnetic transition

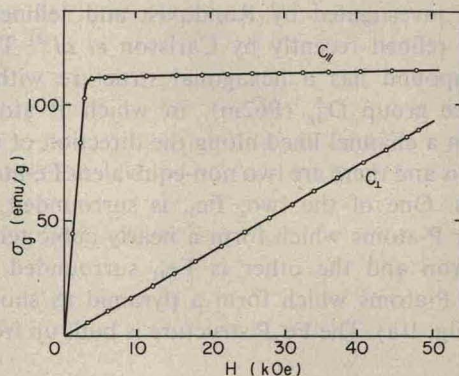


Fig. 2. Magnetization curves along the direction parallel and perpendicular to the *c* axis at 4.2 K.

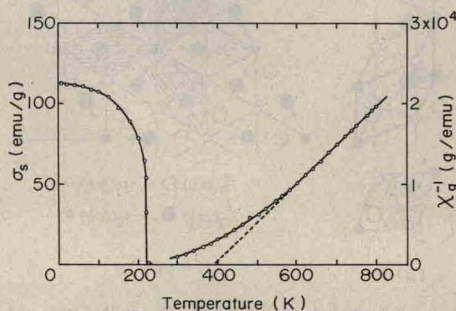


Fig. 3. Magnetic moment, σ_g , and inverse susceptibility, χ_g^{-1} , plotted against temperature.

at the Curie temperature is of the first order as mentioned from the result of the Mössbauer experiment by Wäppling *et al.*⁷⁾ and also as being clear from our measurements of the thermal expansion and the electrical resistance which will be described latter. But the well-defined jump of the magnetization due to the first-order transition cannot be seen in the magnetization vs temperature curve, although it is observed in the temperature dependences of the thermal expansion and the electrical resistance. This may be due to the induced magnetic moments by external field as mentioned by Grazhadankina *et al.*¹⁴⁾ in MnAs compound. The ferromagnetic to paramagnetic transition may be accompanied by the first-order transition with a lattice distortion.

Figure 4 shows the temperature dependence of the magnetization near the Curie temperature at various magnetic fields. The magnetization is almost constant below the Curie temperature and decreases abruptly near the Curie temperature. We therefore determined the ferromagnetic to paramagnetic transition temperatures by the inflection points of these curves. The magnetic transition temperature increases linearly with increasing field as shown in Fig. 4. The Curie temperature T_c was determined by the extrapolation of the magnetic transition temperature to zero field and then $T_c = 208.6$ K was obtained. The value of T_c thus determined is in good agreement with that obtained by Wäppling *et al.*⁷⁾ The paramagnetic susceptibility obeys the Curie-Weiss law in the higher temperature region as shown in Fig. 3. The paramagnetic Curie temperature is 395 K which is by about 200 K higher than T_c . The effective number of Bohr magneton is $3.39 \mu_B$ per Fe atom, which is larger than $2.79 \mu_B$ by Meyer and Candeville⁴⁾ and $3.2 \mu_B$ by Chiba,³⁾ but

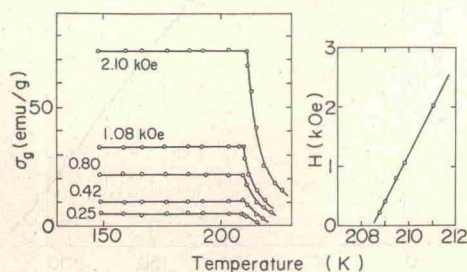


Fig. 4. Temperature dependence of the magnetization near the Curie temperature at various magnetic fields.

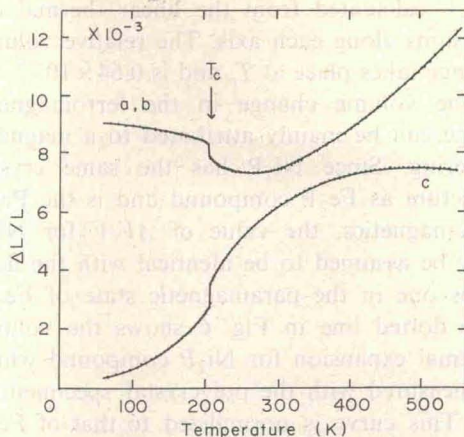


Fig. 5. Temperature dependence of the linear thermal expansion along the a , b and c axes.

smaller than $3.60 \mu_B$ by Nagase *et al.*¹⁵⁾

Figure 5 shows the temperature dependences of the linear thermal expansions along the a , b and c axes. In the ordered region, the relative length along the a and b axes, $(\Delta l/l)_a$ and $(\Delta l/l)_b$ decrease with increasing temperature, while that along the c axis, $(\Delta l/l)_c$ increases with increasing temperature. The thermal expansions along all the directions at T_c reveal the discontinuity which indicates that the ferromagnetic-paramagnetic transition is accompanied by the first-order transition of the lattice distortion as mentioned above. In this discontinuity there are the contraction of 0.74×10^{-3} for the a and b axes and the expansion of 0.84×10^{-3} for the c axis at T_c . In the disordered region, $(\Delta l/l)_a$ and $(\Delta l/l)_b$ are concave and $(\Delta l/l)_c$ is convex against temperature. Figure 6 shows the volume thermal expansion

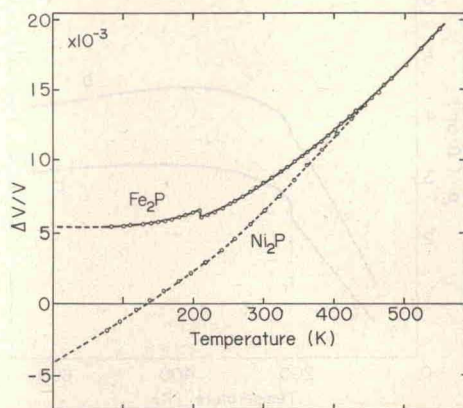


Fig. 6. Temperature dependence of the volume thermal expansion.

$\Delta V/V$ calculated from the linear thermal expansions along each axis. The relative volume change takes place at T_c and is 0.64×10^{-3} .

The volume change in the ferromagnetic range can be mainly attributed to a magnetic ordering. Since Ni_2P has the same crystal structure as Fe_2P compound and is the Pauli paramagnetics, the value of $\Delta V/V$ for Ni_2P may be assumed to be identical with the fictitious one in the paramagnetic state of Fe_2P . The dotted line in Fig. 6 shows the volume thermal expansion for Ni_2P compound which is measured with the polycrystal specimen by us. This curve is normalized to that of Fe_2P at 550 K, at which the paramagnetic susceptibility of Fe_2P begins to follow the Curie-Weiss law. The difference between the values of $\Delta V/V$ of Fe_2P and Ni_2P is considered to be indicative of the exchange striction caused by a magnetic ordering as shown in Fig. 6. The exchange striction at 0 K obtained from the extrapolation of each curve to 0 K and its value is estimated as 9.5×10^{-3} .

Figure 7 shows the temperature dependences of the electrical resistivities along the b and c axes. The change of the resistivity associated with the spin disorder in ferromagnetic region is larger along the b axis than along the c axis. Along each direction there is a rapid increase of the resistivity at T_c . This indicates that the first-order transition takes place at T_c . In the paramagnetic range, the resistivity along each axis decreases slightly with increasing temperature.

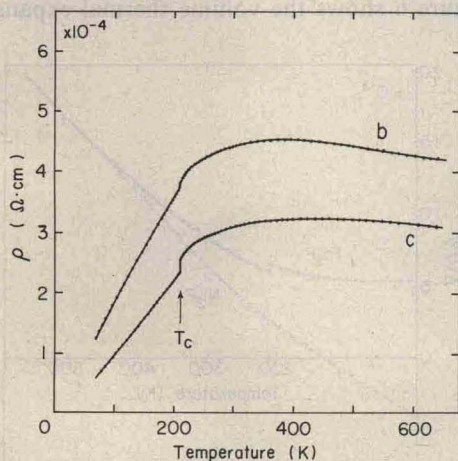


Fig. 7. Temperature dependence of the electrical resistivity along the b and c axes.

§4. Discussion

For a hexagonal crystal in the ferromagnetic state, the magnetocrystalline anisotropy is generally expressed by

$$E = K_1 \sin^2 \theta + K_2 \sin^4 \theta + \dots, \quad (1)$$

where K_1 and K_2 are the first- and second-order anisotropy constants, respectively, and θ is the polar angle of the magnetization vector to the c axis. From the minimum condition of the free energy containing the Zeeman energy, the following equation can be obtained.

$$\frac{H}{M} = \frac{2K_1}{M_s^2} + \left(\frac{4K_2}{M_s^4} \right) M^2, \quad (2)$$

where M_s is the saturation magnetization and M is the magnetization along the direction perpendicular to the c axis in the effective field, H . The anisotropy constants K_1 and K_2 were determined from measurements of M_s and M by the use of eq. (2). Since M is proportional to H as seen in Fig. 2, K_2 is negligibly small. Figure 8 shows the temperature dependence of K_1 . The value of K_1 is 2.32×10^7 erg/cm³ at 4.2 K and considerably larger than those in the other 3d-transition ferromagnetic compounds. According to Zener's theory,¹⁶⁾ the temperature dependence of K_1 would seem to be represented by the fifth power function of the saturation magnetization except for in the vicinity of the Curie temperature as shown by the dashed line. We calculated the anisotropy constant K_d due to the magnetic dipole-dipole interaction by

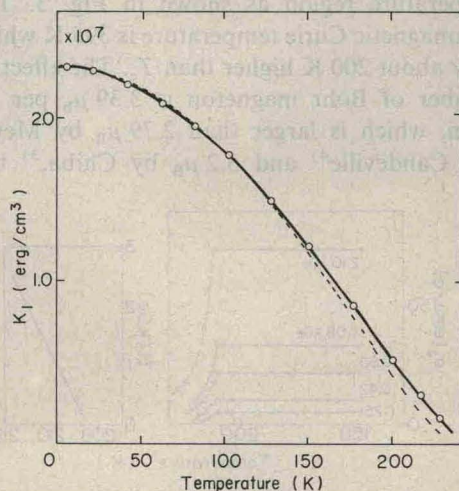


Fig. 8. Temperature dependence of the anisotropy constant.

taking into account the neighboring Fe-atoms up to the 6th nearest. The calculated value was estimated as 4.0×10^5 erg/cm³ at 0 K. The temperature dependence of K_1 taken into account K_d do not obey the third power function supposed for the crystalline field anisotropy. The value of K_1 may be due to the anisotropic exchange as well as the crystalline field anisotropy.

Since the ferromagnetic-paramagnetic transition at T_c is accompanied by the first order transition with a lattice distortion, the pressure variation of T_c , $\Delta T_c/\Delta p$, has to satisfy the thermodynamical Clausius Clapeyron equation;

$$\frac{\Delta T_c}{\Delta p} = \frac{\Delta V}{\Delta S}, \quad (3)$$

where ΔS and ΔV are the discontinuous jumps in the entropy and the volume at T_c , respectively. We have measured the variation of T_c under the hydrostatic pressures up to 6 kbar and obtained as $\Delta T_c/\Delta p = -3.46 \times 10^{-3}$ deg/bar. Using the value of ΔV obtained in this experiment, the magnitude of ΔS is estimated as 0.04 cal/mol·deg, which is relatively small for a first-order transition.

According to Rodbell and Bean,¹⁷⁾ if the exchange interaction which give rise to the magnetic ordering strongly depends upon the interatomic spacing, the Curie temperature T_c is expressed by the following equation,

$$T_c = T_0 \left(1 + \beta \frac{V - V_0}{V_0} \right), \quad (4)$$

where V_0 is the specific volume in the absence of exchange interaction, T_0 the Curie temperature of the rigid lattice and β the ratio between the changes of T_c and volume. On the basis of the molecular field approximation, the exchange striction at 0 K from the equilibrium condition is given by

$$\left(\frac{V - V_0}{V} \right) = \frac{3}{2} \frac{j^2}{j(j+1)} NkKT_0\beta. \quad (5)$$

Where j is the total angular momentum, K is the compressibility, N is the number of magnetic atoms per unit volume, k is the Boltzman constant. Here, if we define the parameter as

$$\eta = 40NkKT_0\beta^2 [j^2(j+1)^2 / (2j+1)^4 - 1], \quad (6)$$

we notice that for $\eta < 1$ the transition is of second order, while for $\eta > 1$, the transition is

of first order. If the ferromagnetic-paramagnetic transition is of first order, the volume change at T_c is given by

$$\left(\frac{\Delta V}{V} \right) = \frac{3}{2} \frac{j^2}{j(j+1)} NkKT_0\beta\sigma_c^2, \quad (7)$$

where σ_c is the jump of the relative magnetization at T_c . Also, the pressure variation of the Curie temperature can be derived from eq. (4) as,

$$\frac{\partial T_c}{\partial p} = -\beta KT_0. \quad (8)$$

We can estimate the exchange striction at 0 K and the volume change at T_c from eqs. (5), (6), (7) and (8). On substituting the value of K , T_0 , and $\Delta T_c/\Delta p$ into eq. (8), we have the value of $\beta = 28.8$. Here, we used the value of $K = 4.8 \times 10^{-13}$ cm²/dyne for Fe₂P measured by means of the X-ray diffraction under high pressure, which will be reported in near future, the value of $T_0 = 250$ K obtained by extrapolating the Brillouin function curve for $j = \frac{3}{2}$ to zero magnetization. On substituting the values of $\beta = 28.8$ and $j = \frac{3}{2}$ deduced by the magnetization at 0 K in eq. (6) we have $\eta = 1.20$. This suggests that the transition at T_c is of first order. The exchange striction at 0 K and the jump of volume at T_c are estimated to be 9.1×10^{-3} and 1.6×10^{-3} , from eqs. (5) and (7), respectively. Here, the value of σ_c was used 0.44 obtained from the jump of the hyperfine field at T_c determined by Wäppling *et al.*¹¹⁾ These estimated values are in reasonable agreement with the experimental values of 9.5×10^{-3} and 0.64×10^{-3} , respectively. In conclusion, the ferromagnetic to paramagnetic transition at T_c of Fe₂P might be accompanied by the first-order transition with a lattice distortion due to magnetoelastic effects.

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