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The weak field ac susceptibiltiy and the resistivity of Fe_2P single crystals were measured as functions of temperature from 4.2–300 K and as functions of hydrostatic pressures up to 20 kbar, using a newly designed clamp-type pressure cell. The Curie temperature, and the first-order transition temperature, decreased rapidly with increasing pressure, and ferromagnetism vanished at about 13 kbar at 0 K. A second-order transition temperature, as well as the first-order transition, appeared in the region below 170 K and above 5 kbar (triple point) and a new pressure-induced magnetic phase was found. The phase is proposed to be antiferromagnetic for reasons discussed in the paper.

1. Introduction

A study of pressure-induced magnetic phase transitions seems to be valuable for a basic understanding of magnetic materials, since the variation of lattice parameter or volume induced by pressure may control the electronic structure with some advantages over the usual alloying effect, in which the various magnetic phases can be controlled by varying the composition.

In this respect iron phosphide Fe_2P, the magnetic and crystallographic characteristics of which have been extensively investigated [1–7], would be one of the most appropriate materials to be investigated for the following reasons. (i) The transition at the Curie temperature T_c is of first order. (ii) According to Goodenough et al. [5], referred to as [G] hereafter, T_c decreased rapidly with increasing pressure, and they have suggested a pressure-induced transition at 0 K from a ferromagnetic to metamagnetic state at about 13 kbar. (iii) A recent thorough investigation by Lundgren et al. [7], referred to as [L] hereafter, of non-stoichiometric $Fe_{2-x}P$ as well as of stoichiometric Fe_2P has shown that an increase in x, or an increase in the number of introduced vacancies caused a rapid decrease in T_c and suggested the appearance of metamagnetic phase. (iv) Fruchart et al. [3] have found in a system $(Fe_{1-x}Mn_x)_2P$ that a very small substitution of manganese for iron into Fe_2P may induce the metamagnetism. The present authors et al. [8] have recently found the existence of an antiferromagnetic region in the same system.

In view of the results given above, we have investigated the pressure–temperature magnetic phase diagram of Fe_2P by measurements of the weak field ac susceptibility and the resistivity, using single crystal specimens. The hydrostatic pressure was generated up to 20 kbar in a clamp type pressure cell and the measurements were made from 300 K down to 4.2 K. As a result, a new pressure-induced phase was found.

2. Experimental

Single crystal specimens were cut out from the single crystal ingot. The compound was prepared by solid–vapour reaction, and the single crystal was grown by thermal annealing. Details of the preparation have been described by Fujii et al. [6] referred to as [F] hereafter. The specimens were the c-axis rectangular rods of $1 \times 1 \times 2$ mm^3 for the measure-

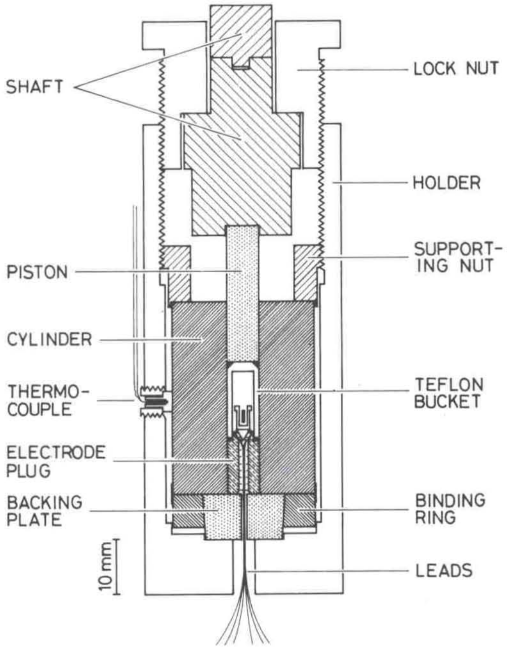

Fig. 1. Cross section of high pressure clamp cell, designed for pressures up to 30 kbar.

ments of both susceptibility and resistivity.

The pressure was generated with a simple clamp type piston–cylinder apparatus which was designed by some of the present authors [9]. Since the details will be separately described elsewhere, only the principles are given in the present paper. Fig. 1 shows a cross section of the pressure cell. The shaft, piston and cylinder were made of hardened alloy steel, WC and hardened Be–Cu, respectively. The cylinder was hydraulic autofrettage processed. As a result, the maximum working hydrostatic pressure was elevated to 30 kbar at room temperature. The pressure transmitting medium was a mixture of 1 : 1 n-pentane and isoamyl alcohol. The above-mentioned pressure generating assembly was inserted inside the holder, which also serves as a protector. At that time the settlement of the assembly was accomplished by the supporting nut and the backing plate with the binding ring. The sample cavity consists of a teflon bucket and Be–Cu electrode plug. The seal of the plug was provided by means of single cone sealing.

Except near 4.2 K, the manganin wire was used as a pressure gauge. The gauge was loosely wound on a bakelite bobbin glued on the cone. The calibration of

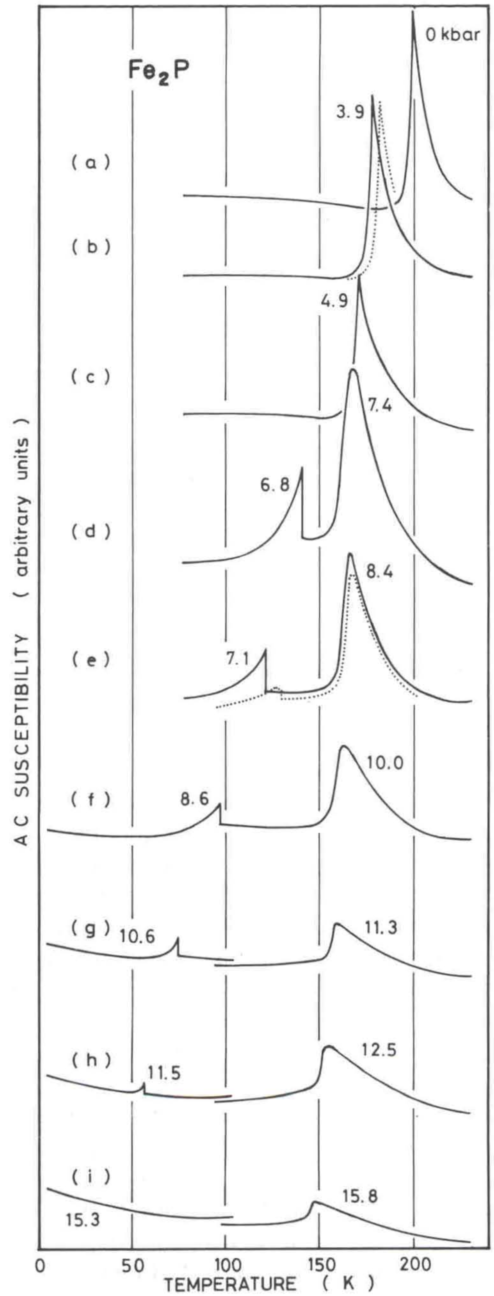

Fig. 2. AC susceptibility χ in arbitrary unit versus temperature under various pressures for Fe_2P. The details are described in the text.

the gauge was accomplished at room temperature by measuring the transition pressure of Bi I → II, 25.4 kbar. The pressures at lower temperatures were deter-

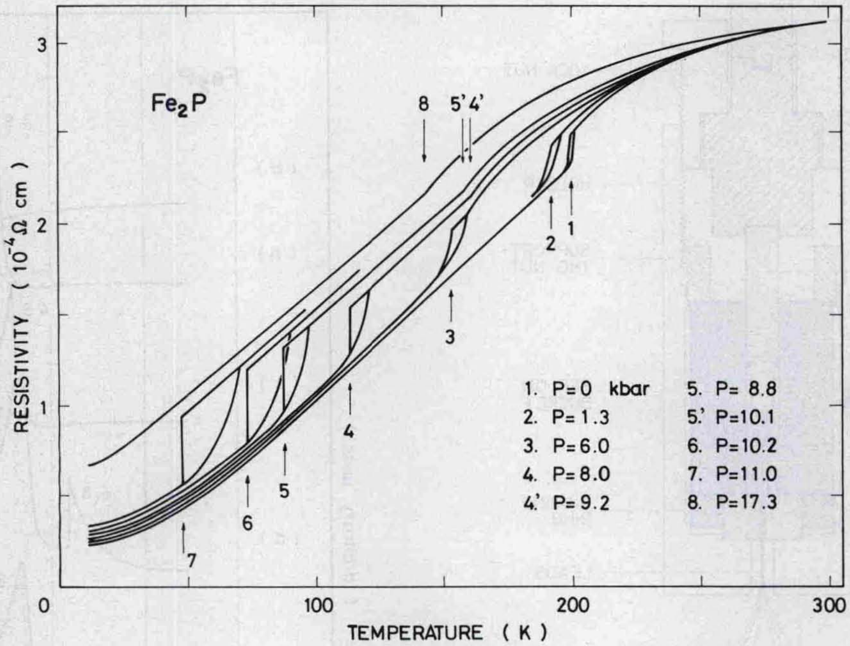

Fig. 3. Resistivity ρ versus temperature under various pressures for Fe_2P. The arrows with appended numbers in the figure indicate the locations of the transition temperatures. The pressures at respective transition temperatures are given in the right hand corner of the figure.

mined by taking into account the pressure drop during cooling, which was estimated from the observed results of the temperature dependence of the manganin resistance at different pressures. Practically, the pressure value initially determined at room temperature decreased almost linearly with temperature and became almost constant after freezing of the pressure medium. The pressure near 4.2 K was determined by measuring the shift of the superconducting transition temperature of Sn with pressure.

The ac susceptibility χ was measured by means of a Hartshorn bridge under the magnetic field applied along the *c*-axis. The amplitude and the frequency of the field were 0.1 Oe and 1 kHz, respectively. The electrical resistivity was measured along the *c*-axis with a standard four-probe method. Both measurements were made in a temperature range from 300 K down to 4.2 K. The temperature was lowered or raised at a rate of one degree per five to six minutes, and the experimental points were at intervals of one degree, so the results will not be plotted but drawn as a curve in the subsequent figures, figs. 2 and 3. The AuFe–Chromel thermocouple or Ge resistor was installed through a hole in the holder as indicated in fig. 1. For the measurements at lower temperatures, the whole assembly was transferred and placed in the thermal insultating chamber.

3. Results

3.1. Susceptibility measurement

Fig. 2 shows the variation of χ in arbitrary units in the temperature decreasing run under various pressures. In the figure, curve (a) indicates the result at atmospheric pressure, $p = 0$ kbar, and the pressure increases in a descending order from curve (b) to cruve (i). As is evident from the figure, there are well-defined peaks, indicating magnetic transitions, so that the magnetic transition temperature in the present work was defined as a peak temperature in the temperature decreasing run, as given by the solid curve. As described in the previous section, the pressure decreases during the temperature decreasing run, so that all the curves are not isobaric. Near the peaks, the estimated pressures at the peaks are denoted by the figures in units of kbars.

The results shown in the figure are arranged as follows. (i) The magnetic transition, T_c, at $p = 0$ kbar takes place at 200 K [curve (a)]. (ii) In the case of curve (b), the thermal hysteresis associated with the transition is also illustrated, where a dotted curve represents the temperature increasing run. The width of the hysteresis is 4 K. (iii) In the curves from (d) to (h), two peaks at high and low temperatures are clearly discriminated. The temperature increasing run is shown also in (e) and there is a thermal hysteresis at the low temperature peak. (iv) The sensitivity of the output in the measurements of the curves from (d) to (f), and of high temperature peaks in curves from (g) to (i) was about five times as high as that in the measurements of the curves (a) through (c). In other words, the substantial intensity of the high temperature peak in the curve (d) drastically decreased relative to that in curve (c). From (g) to (i), the sensitivity for the low temperature peaks was about two times as high as that for the high temperature peaks. (v) In curve (i), the low-temperature peak at the low temperature side vanishes. The number 15.3 in the left hand corner is the pressure value in kbar at 4.2 K.

Regarding the assignment of the magnetic transitions, there are two points to be considered. One is the thermodynamical order of the transition. With respect to the χ–T curve, the thermal hysteresis and sharp discontinuity at the peak were regarded as indication of a first-order transition. In this respect, the transitions observed in curves (a), (b) and (c), and those at lower temperatures in (d) through (h) have the characteristics of the first order transitions; in addition, they display a thermal hysteresis which is not shown in fig. 2. On the other hand, the transition at high temperature which appear in curves from (d) to (i) are of second order, judging from the peak shape and the experimental fact that hysteresis phenomena were not observed. Another point to be considered will be described in section 3.3.

3.2. Resistivity measurement

The data on the electrical resistivity under various pressures which are complementary to the susceptibility data are given in fig. 3. The lowest curve indicates the result at $p = 0$ kbar and the pressure increases in an ascending order from the lowest to upper curves. The arrows with appended numbers indicate the locations of transition temperatures, the definition of which will be given below, and the numbers, except those with primes, 4′ and 5′, are also used for the curve number. The pressures at the respective transition temperatures are given in the right hand corner in the figure.

The experimental facts which are obtained from the figure are arranged as follows: (i) in the curve at $p = 0$ kbar, a relatively sharp drop is found at 200 K in the temperature decreasing run and a well-defined thermal hysteresis is also observed. This behaviour in in the ρ–T curve is typical of a first-order transition. The transition temperature, 200 K, defined as a temperature at the beginning of the drop, coincides with the temperature determined by the susceptibility measurement. Therefore, this temperature was taken to be the T_c value at $p = 0$ kbar of the Fe_2P specimen employed. (ii) The situation with respect to the first-order transition in curve 1 is the same in curves 2 through 7, where the hysteresis widths become increasingly large. The definition of transition temperatures is the same as in curve 1. (iii) A small but recognizably new bend appears on the higher temperature side, 4′, in curve 4. This bend may correspond to another transition, and the transition temperature defined by the bend and pressure at the bend were 152 K and 9.2 kbar, respectively. The situation regarding the bend is the same in curves 5, 6 and 7, although the curves around the bends are not shown for the latter two cases. (iv) At 17.3 kbar (curve 8), the bend occurs at 135 K, but by 16.9 kbar the first-order transition could not be detected down to 10 K. Regarding the bends observed, the transition at the bend should be of second order, since there is no hysteresis. (v) With respect to the drop in the temperature decreasing run, it should be mentioned that the sharpness of the drop is rather weak in curve 3, but the drops are very sharp in curves from 4 to 7.

Furthermore, the appearance of two peaks in χ–T curves in fig. 2 presumably corresponds to the appearance of the very sharp drop and the bend in ρ–T curves in fig. 3. On this basis, the order of the high- and low-temperature phase transitions in χ and ρ have been assigned consistently. As a whole, the resistivity measurement is more appropriate for the confirmation of the first-order transition as well as for the determination of the transition temperature. On the other hand, the suscpetibility measurement is better for the determination of the second-order transition temperature.

3.3. *Pressure-temperature magnetic phase diagram*

The transition temperatures determined in figs. 2 and 3 are plotted in fig. 4 as a pressure–temperature magnetic phase diagram. The closed and open symbols stand for the results obtained from the susceptibility and resistivity measurements, respectively. The circles and squares are the first- and second-order transitions, respectively.

Another point to be considered with respect to the magnetic transition is the assignment of the magnetic phases of the three regions, I, II and III in fig. 4. It was made on the basis of the following considerations. Region I: since Fe_2P at atmospheric pressure is ferromagnetic at temperatures below T_c, region I should be ferromagnetic, and all the first-order transition temperatures, therefore, are designated as T_c's.

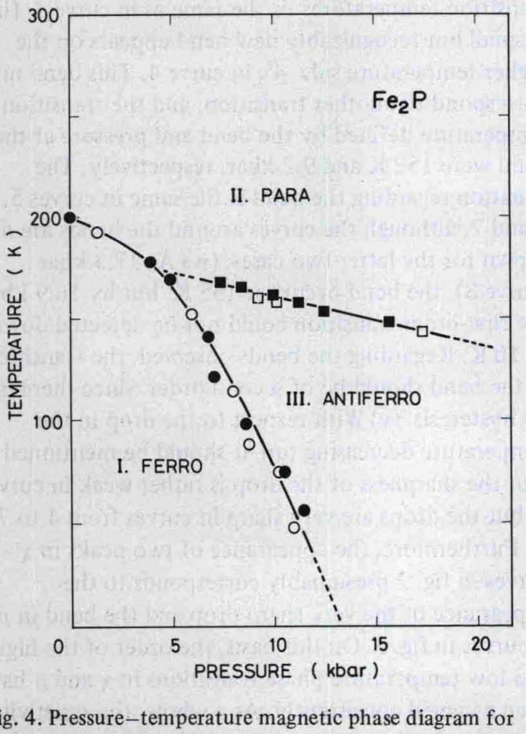

Fig. 4. Pressure–temperature magnetic phase diagram for Fe_2P. ● and ■, susceptibility data; ○ and □, resistivity data.

Region II: Region II should be paramagnetic. Region III: this region, which has been clarified in the present work, is a pressure-induced phase. [G] has suggested a pressure-induced transition to a metamagnetic state on the basis of their results of the dependence of pressure on T_c up to 11 kbar and have estimated the critical pressure, at which the ferromagnetism vanishes at 0 K, as about 13 kbar. [L] has thoroughly investigated the effect on non-stoichiometry by observing the x-dependence of T_c of $Fe_{2-x}P$ ($0 < x \leqslant 0.06$), and assumed that the magnetic states for $x > 0.04$ is metamagnetic. Furthermore, they took notice of the similarity of the effect of non-stoichiometry to the pressure effect obtained by [G], from the standpoint of the volume contraction due to the introduced vacancies. Fruchart et al. [3] have found in the system $(Fe_{1-x}Mn_x)_2P$ that a very small substitution of manganese into Fe_2P may induce the metamagnetism. Also, the magnetic phase diagram for $0 < x \leqslant 0.05$ obtained by the present authors et al. [8] has established the existence of an antiferromagnetic phase bounded by T_c and T_N (Néel temperature) lines. The magnetic phase diagram seems to be analogous to fig. 4, although the abscissa is not pressure p, but manganese concentration x. Under these circumstances, we might suggest that region III is antiferromagnetic and the second-order phase transition tempertures are therefore T_N's. To establish definitively region III is antiferromagnetic, measurements of the magnetization and of neutron diffraction under pressure should be made, and the former measurement is now in progress.

On the basis of the above-mentioned assignment, the important results in fig. 4 are summarized as follows. (i) When the pressure is larger than about 5 kbar, the rate of decrease in T_c becomes larger and the decrease tends to be rather linear, indicating that the critical pressure at 0 K is about 13 kbar by extrapolating the T_c versus pressure curve. This value of critical pressure is not inconsistent with that suggested by [G]. The initial gradient of the curve at $p = 0$ kbar, $\Delta T_c/\Delta p$, was defined in the present work as the gradient of a line connecting T_c values at $p = 0$ and 1.3 kbar, and it was about -5.4 K kbar^{-1}. [F] also have measured T_c under hydrostatic pressure up to 6 kbar. The data $\Delta T_c/\Delta p$ reported by [F] and [G] are -3.46 and about -4 K kbar^{-1} respectively for polycrystal speciments having T_c values of 208.6 and 221 K. (ii) T_N decreases almost linearly with increasing pressure. The rate of decrease is about -2.4 K kbar^{-1} which is considerably smaller in magnitude than that of T_c, -23 K kbar^{-1}, in the same pressure range. (iii) There is a triple point of para–antiferro–ferromagnetic states and it is established at about 5 kbar and 170 K.

4. Discussion

An initial qualitative discussion will be given using the arguments of Bean and Rodbell [10] regarding the order of the magnetic phase transition when the exchange interaction strongly depends on the interatomic distance. According to them, the generalized requirement for a first-order transition under a pressure p is given by

$$\eta + p\kappa\beta > 1. \tag{1}$$

As is evident, the requirement at atmospheric pressure is $\eta > 1$. In eq. (1), κ is the compressibility, η a quantity which is proportional to $T_0\kappa\beta^2$ and $\beta[=\mathrm{d}(T_c/T_0)/\mathrm{d}(V/V_0)]$ is estimable from eq. (2)

$$\Delta T_c/\Delta p = -\beta\kappa T_0. \tag{2}$$

The temperature T_0 is the Curie temperature of the rigid lattice without lattice distortion. The estimated value of η at $p = 0$ kbar according [F] was 1.2, using their estimated value of $T_0 = 250$ K and the value of κ which was measured by means of X-ray diffraction under pressure [11] *. Although the result is rather qualitative. the left-hand side of eq. (1) is expected to become large as p increases, since β is positive. As a result, both the discontinuous drop and the hysteresis width at the first-order transition temperature are expected to become large and the transition becomes sharp. The experimental results shown in fig. 3 are seen to reflect these properties.

We will next discuss the pressure dependences of T_c and T_N from the standpoint of the magnetic coupling, since the existence of ferro- and antiferromagnetic regions under pressure depends on the pressure dependence of the competition between ferro- and antiferromagnetic couplings.

In Fe_2P, a hexagonal structure with a space group $D^3_{3h}(P\bar{6}2m)$, there are two non-equivalent sites for Fe atoms: the tetrahedral and pyramidal sites, denoted in the present paper by sites 1 and 2, respectively. On the basis of the pair interaction model, therefore, T_c of Fe_2P at atmospheric pressure can be expressed as [12]

$$T_c = 2T_{11} + 4T_{12} + 4T_{22}, \tag{3}$$

where T_{11} and T_{22} stand for the magnetic coupling energy in units of degrees between Fe atoms at sites 1 and 2 respectively, and T_{12} represents the energy between the Fe pair at sites 1 and 2. The values of T_{ij} have been estimated from the x-dependence of T_c in the system $(Fe_{1-x}Ni_x)_2P$ [12] and they are *: $T_{11} = -625$ K, $T_{12} = 450$ K and $T_{22} = -85$ K. Among the T_{ij}'s given above, the term T_{22} with relatively small magnitude might be less sensitive to pressure, since (i) the distance between 2–2 sites is relatively large in comparison with those between 1–1 sites and sites 1 and 2, and (ii) the magnetic moment of 3d electrons of the Fe atom at site 2 may have a localized character, as was pointed out from a neutron diffraction study of single crystal Fe_2P [13]. With respect to the pressure dependence of the competition between ferro- and antiferromagnetic states, the antiferromagnetic coupling overcomes the ferromagnetic one beyond the triple point in any case, but there are several possibilities for the pressure dependences of T_{11} and T_{12}. For a more definitive conclusion, the following analysis and experiment would be required. (i) An analysis in which the magnetic entropy term is taken into accoun should be made theoretically, and (ii) experimental data on the effect of uniaxial pressure on the transition temperatures would be worthwhile since the pressure effect on T_{11} and T_{12} might reflect the variation of the lattice constants with pressure along the c-axis and the a-axis, respectively.

In terms of the itinerant electron model, Goodenough [14] tried to interpret the pressure effect on T_c of Fe_2P in [G] by means of his conceptual phase

* The technique will be referred to by Yamamoto et al. in ref. [11].

* The values of T_{ij} in the present paper are corrected values, since eq. (4), the expression for the x-dependence of T_c, was given incorrectly in ref. [12].

diagram for quarter-filled, twofold bands of correlated electrons. The essential quantities introduced by him are the correlation energy U and band width w. The magnitude of w increases with increasing pressure, as has generally been accepted, and U, which was defined by Goodenough as the Weiss molecular field energy, decreases with pressure. As a result, T_c decreases rather rapidly and the antiferromagnetic state tends to be stabilized relative to the ferromagnetic state. It seems, therefore, that our experimental results just explain this circumstance. In the investigation of the pressure effect on T_c in the system of $MnAs_xSb_{1-x}$, Edward and Bartel [15] made an analysis of the first- and second-order transitions. There they have pointed out that, depending upon the amount of magnetoelastic coupling, the rate of change in w with pressure determines the order at the transition. When the s-band as well as d-band cross the Fermi level, another basic quantity for analyzing $\Delta T_c/\Delta p$ such as the s–d transfer [16,17] would also be required.

Although a definite interpretation has not been made regarding all aspects of the present work, the following results and arguments will be helpful to our future analysis. (i) The preferred site for both vacancy in non-stoichiometric $Fe_{2-x}P$ [18] and non-magnetic manganese in $(Fe_{1-x}Mn_x)_2P$ [3] is site 2. (ii) The increase in resistivity ρ at T_c in fig. 3, which results from the transition from ferro- to antiferromagnetic states, may come from a complex spin configuration in the antiferromagnetic state. (iii) Pressure-induced antiferroelectricity in ferroelectric CsH_2PO_4 observed by Yasuda et al. [19]. In this case, there are two peaks in the temperature dependence of the relative permittivity under pressure. This phenomena is very similar to the present one, and the analysis made by Yasuda et al. seems to be very suggestive.

Finally, a comment will be made on the effect of the T_c value of the employed specimen on the pressure dependence. [L] have pointed out that for Fe_2P the sample preparation requires a delicate technique and it is rather difficult to define a unique T_c value. The value of T_c obtained in the pressure experiments in [G] is 221 K. In the present work, therefore, thorough experiments were also carried out on another specimen, for which the T_c value was 194 K. The experiment showed, however, that no recognizable modification was required for the phase diagram in fig. 4.

It may safely be concluded that the pressure–temperature magnetic phase diagram presently obtained is appropriate for Fe_2P. The successful detection of the second-order transition temperature may possibly be due to the employment of a single crystal and to the complementary measurements of the susceptibility and resistivity.

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