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 inter-atomic 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 $\beta[=d(T_c/T_0)/d(V/V_0)]$ 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 antiferro-magnetic regions under pressure depends on the pres-

sure dependence of the competition between ferro- and antiferromagnetic couplings.

In Fe_2P, a hexagonal structure with a space group $D_{3h}^3(P\bar{6}2m)$, 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 ferro-magnetic 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 tempera-tures 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, Goode-nough [14] tried to interpret the pressure effect on T_c of Fe_2P in [G] by means of his conceptual phase

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* 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 nonmagnetic 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.

Acknowledgement

References

[1] S. Chiba, J. Phys. Soc. Japan 15 (1960) 581.
[2] A.J.P. Meyer and M.C. Cadeville, J. Phys. Soc. Japan Suppl. B-1 17 (1962) 223.
[3] R. Fruchart, A. Roger and J.P. Senateur, J. Appl. Phys. 40 (1969) 1250.
[4] B. Carlsson, M. Gölin and R. Rundqvist, J. Solid State Chem. 8 (1973) 57.
[5] J.B. Goodenough, J.A. Kafalas, K. Dwight, N. Menyuk and A. Catalano, AIP Conf. Proc. 10 (1973) 1355.
[6] H. Fujii, T. Hōkabe, T. Kamigaichi and T. Okamoto, J. Phys. Soc. Japan 43 (1977) 41.
[7] L. Lundgren, G. Tarmohamed, O. Beckman, B. Carlsson and S. Rundqvist, Phys. Scripta 17 (1978) 39.
[8] T. Okamoto et al., to be published.
[9] H. Fujiwara, H. Kadomatsu and K. Tohma, Rev. Sci. Instr. (1980) to be published.
[10] C.P. Bean and D.S. Rodbell, Phys. Rev. 126 (1962) 104.
[11] H. Fujiwara et al., to be published; Y. Yamamoto, M. Nomura and H. Fujiwara, Japan. J. Appl. Phys. 16 (1977) 397.
[12] H. Fujii, T. Hōkabe, H. Fujiwara and T. Okamoto, J. Phys. Soc. Japan 44 (1978) 96.
[13] H. Fujii, S. Komura, T. Takeda, T. Okamoto, Y. Ito and J. Akimitsu, J. Phys. Soc. Japan 46 (1979) 1616.
[14] J.B. Goodenough, J. Solid State Chem. 7 (1973) 428.
[15] L.R. Edwards and L.C. Bartel, Phys. Rev. B5 (1972) 1064.
[16] N.D. Lang and H. Ehrenreich, Phys. Rev. 168 (1968) 605.
[17] H. Fujiwara, H. Kadomatsu, K. Ohishi and Y. Yamamoto, J. Phys. Soc. Japan 40 (1976) 1010.
[18] R. Wäppling, L. Häggström, T. Ericsson, S. Devanarayanan, E. Karlsson, B. Carlsson and S. Rundqvist, J. Solid State Chem. 13 (1975) 258.
[19] N. Yasuda, M. Okamoto, H. Shimizu and S. Fujimoto, Phys. Rev. Lett. 41 (1978) 1311.