PRESSURE VARIATION OF THE CURIE TEMPERATURE AND SPONTANEOUS MAGNETIZATION IN Fe_2P AND $Fe_2P_{0.9}As_{0.1}$*

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ABSTRACT

The transition-metal pnictides $(M_{1-y}M'_y)P_{1-x}As_x$ exhibit structural relationships and magnetic properties that indicate the presence of filled valence bands, empty conduction bands, and partially filled 3d bands active in metal-metal bonding. In many cases they support spontaneous magnetism, thereby offering the opportunity to study itinerant-electron magnetism as a function of 3d bandwidth and occupancy. In particular, the hexagonal system $Fe_2P_{1-x}As_x$ is ferromagnetic, but for $x < 0.33$ its spontaneous moment at T = 0K is reduced from the $\mu_o = 3.0\mu_B$/molecule predicted for itinerant, spin-only ferromagnetism. We investigated the pressure dependence of T_c and μ_o to 11 kbar. In Fe_2P, the relation between ΔT_c [° C] and P [kbar] is: $P = -0.252(\Delta T_c) - 0.0012(\Delta T_c)^2$. In $Fe_2P_{0.9}As_{0.1}$, it is: $P = -0.71(\Delta T_c) - 0.0017(\Delta T_c)^2$. Pressure did not change significantly the value of μ at 58K, but it promoted a remarkably exchange-enhanced susceptibility above T_c. We interpret these results to mean that the reduced moment in Fe_2P is not due to conduction-band overlap of the Fermi energy, but to a 3d bandwidth that is just narrow enough to support spontaneous ferromagnetism. A critical pressure $P_c \approx 13$ kbar is estimated for a ferromagnetic-to-metamagnetic transition.

INTRODUCTION

Transition metals (M) and their alloys are characterized by narrow 3d bands that are overlapped by a broad 4s band. In the pnictides M_2X, introduction of the X atoms splits the broad bands into a valence band and a conduction band that are separated by a finite energy gap. If the Fermi energy E_F falls in this gap, then the number z_d of 3d electrons per M atom can be inferred from the formal valence X^{3-}. The absence of X-X pairing, even where M = Ni, and an average formal valence of only 1.5+ at the M atoms, indicate that the broad valence bands are filled. In order to establish that the broad conduction band is empty, it is useful to have a theoretical prediction for the magnitudes of the atomic moments as a function of z_d for an itinerant-electron ferromagnet.

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Where M-M bonding via 3d electrons contributes a binding energy that is small compared to intraatomic-exchange stabilization, there the atomic moments at the M atoms can be deduced from crystal-field theory, and the Weiss molecular fields are given by superexchange (or double-exchange) perturbation theories. Where this condition is not fulfilled, an itinerant-electron model of ferromagnetism is generally employed. In this model, both intraatomic and interatomic exchange interactions contribute to the Weiss molecular field. As discussed more fully elsewhere,[1] the celebrated Slater-Pauling curve for the spontaneous magnetization vs electron/atom ratio of the ferromagnetic transition metals and their alloys can be successfully rationalized if it is assumed that the binding energy, being stronger than any magnetic energy associated with the Weiss molecular field, keeps the bonding orbitals occupied. With this assumption, the maximum ferromagnetic moment per M atom contributed by unpaired electron spins in a ν-fold degenerate band is $(\nu/2)\mu_B$, which occurs where the bands are one-quarter or three-quarters filled. The ferromagnetic moment falls off linearly to zero for empty, half-filled, and full bands. However, antiferromagnetism may be associated with a half-filled band, and the atomic moments to be associated with antiferromagnetic order are not predictable from these simple considerations. Finally, since any orbital contribution to the atomic moment is relatively small for itinerant electrons, it follows that fivefold-degenerate 3d bands ($\nu = 5$) should exhibit a maximum atomic moment μ_A (max) $\approx 2.5\mu_B$ at $z_d = 7.5$ and that $d\mu_A/dz_d = +1\mu_B$ for $5 < z_d \leqslant 7.5$, $d\mu_A/dz_d = -1\mu_B$ for $7.5 \leqslant z_d \leqslant 10$. In the system $Fe_2P_{1-x}As_x$, filled valence and empty conduction bands would leave a $z_d = 6.5$, and the predicted spin-only molecular moment for ferromagnetic coupling and $\nu = 5$ would be $\mu_o = 3.0\mu_B$, corresponding to an average $1.5\mu_B$ per Fe atom.

Pure samples of Fe_2P exhibit a $\mu_o = 2.20\mu_B$, noticeably reduced from the predicted spin-only value of $3.0\mu_B$.[2,3] Such a reduction implies either a smaller z_d (due to an overlapping conduction band) or a 3d band that is too broad for the Weiss molecular field to empty all the antibonding states of antiparallel spin. Substitution of As for P increases the M-M separation, thereby reducing the widths of the 3d bands. It also increases the covalent mixing, thereby raising the bottom of the conduction band relative to the 3d bands. Therefore, if the theory outlined above is applicable, then μ_o should increase with x in $Fe_2P_{1-x}As_x$ until it saturates at a $\mu_o = 3.0\mu_B$. This critical experiment has been performed,[2,3] and indeed μ_o saturates at $3.0\mu_B$ for $x \geqslant 0.33$. In order to distinguish whether the reduced moment in Fe_2P is due to conduction-band overlap or to broad 3d bands, we have investigated the pressure dependence of several magnetic properties.

EXPERIMENTAL

The Fe_2P and $Fe_2P_{0.9}As_{0.1}$ samples studied were prepared by direct combination of the elements and were the same as those used for the atmospheric-pressure study.[2] High-pressure measurements were made by

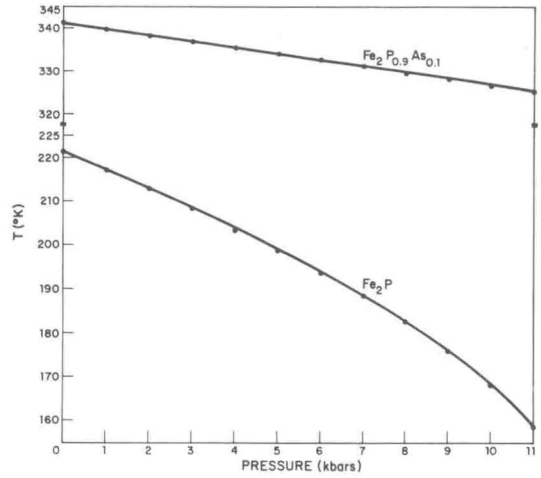

Fig. 1. Pressure dependence of the Curie temperature in Fe_2P and $Fe_2P_{0.9}As_{0.1}$.

using a gas generator with a vibrating-coil magnetometer, as described previously.[4] The Curie-temperatures T_c were obtained at low (100 Oe) fields, and plots of T_c vs hydrostatic pressure P are shown in Fig. 1. The points are experimental, and the solid lines are the analytic functions (with P in kbar and ΔT_c in °C)

$$P = -0.252(\Delta T_c) - 0.0012(\Delta T_c)^2 \text{ for } Fe_2P \quad (1)$$

$$P = -0.71(\Delta T_c) - 0.0017(\Delta T_c)^2 \text{ for } Fe_2P_{0.9}As_{0.1} \quad (2)$$

Extrapolation of eq. (1) to the extremum defined by $\partial P/\partial(\Delta T_c) = 0$ gives a critical pressure $P_c = 13.3$ kbar above which the ground state of Fe_2P should no longer be ferromagnetic.

Surprisingly, there was no significant change with pressure in the magnetization per molecule, μ, at 58K. Examination of μ vs the applied field H at T = 58K showed no appreciable change on passing from 1 atm to 10 kbar pressure. However, measurement of μ vs T/T_c for Fe_2P gave strikingly different results for 1 atm and 10 kbar. At H = 10 kOe, the inflection in μ vs T occurs at $T \approx 1.07\ T_c$ at P = 1 atm, but at $T \approx 1.15\ T_c$ at P = 10 kbar. Furthermore, an extraordinarily large exchange enhancement of the susceptibility, which extends to temperatures well above T_c, is markedly greater at 10 kbar than at 1 atm. At P = 10 kbar and $T = 1.02\ T_c$, a plot of μ vs H is extremely nonlinear, resembling the initial magnetization curve of a ferromagnet at $T < T_c$.

DISCUSSION

If the moment of Fe_2P were reduced from $\mu_o = 3.0\mu_B$ because of conduction-band overlap of E_F, pressure should change z_d, and hence μ_o,

more dramatically than T_c. Therefore, we conclude that the moment of Fe_2P is reduced because the molecular fields are not strong enough to empty all the antibonding states of antiparallel spin.

The existence of antiparallel-spin electrons in the ground state would create a ferromagnetic spin-density wave in the magnetically ordered phase (antiparallel-spin excited electrons create spin waves), and a spin-density wave reflects a long-range antiferromagnetic component to the interatomic-exchange interactions. Since longer M-M separations decrease the width of the 3d bands, the relative importance of this antiferromagnetic component must decrease with increasing As concentration x, which would account for the sharp rise with x in T_c (from 221 to 443K)[2] over the interval $0 \leqslant x \leqslant 0.33$. On the other hand, pressure would increase the antiferromagnetic component, and the critical pressure P_c presumably marks a transition from a ferromagnetic spin-density wave to a metamagnetic state.

The remarkable susceptibility above T_c in Fe_2P, and its enhancement by pressure, would seem to indicate that T_c is suppressed by pressure more rapidly than is the paramagnetic Curie temperature θ. Suppression of T_c relative to θ by weak, long-range antiferromagnetic interactions has been observed[5] in the metamagnetic thiospinel $Zn[Cr_2]S_4$, which contains localized 3d electrons. In Fe_2P, the ferromagnetic short-range order above T_c must be exceptional and appears to extend well above T_c, although the magnetic interactions are three-dimensional. This behavior is quite different from that found in $CoS_{2-x}Se_x$, where the ferromagnetic moment is also reduced because the bandwidth is too large.[6] The $CoS_{2-x}Se_x$ 3d bands are broadened with x, and the ferromagnetic-to-metamagnetic transition is marked by a reduction in θ that makes $\theta < T_c$.[7]

Within the molecular-field approximation, the paramagnetic Curie temperature θ is given by

$$\theta = (2/3k)S(S+1)\sum_v z_{uv} J_{uv} \tag{3}$$

where z_{uv} is the number of v atoms near-neighbor to a u atom. If the interatomic exchange energy falls off more rapidly than linearly with decreasing atomic separation, then

$$J_{uv} \approx \sum_\ell J^o_{uv\ell} \sum_j \left[1 + \beta^j_{uv} \varepsilon_j - \frac{1}{2} (\gamma^j_{uv} \varepsilon_i)^2 + \cdots \right] \tag{4}$$

The $J^o_{uv\ell}$ are components of the uv exchange interaction in the unstrained sample ($P = 0$) and $\beta^j_{uv} > 0$ because an $\varepsilon_j < 0$ increases the 3d bandwidth, thereby lowering J_{uv}. The strain at equilibrium is given by[4]

$$\varepsilon_j = \sum_i K_{ji} \left[\sum_{u,v} (\partial J_{uv} / \partial \varepsilon_i) \vec{S}_u \cdot \vec{S}_v - P + T \sum_k \alpha_k c_{ki} \right] \tag{5}$$

where K_{ji} = cofactor c_{ij}/(determinant c_{ij}), $\vec{S}_u$ and $\vec{S}_v$ are the thermodynamic expectation values of the spins at sites u and v, α_k is a thermal-expansion coefficient, and the c_{ki} are elastic constants. Since μ_o appears to be

relatively independent of pressure, and hence of ϵ_j, the spin quantum number S in eq. (3) is assumed constant. Furthermore, since $|S| = 0$ at $T \geqslant T_c$, it follows that for any temperature $T \geqslant T_c$

$$\frac{\Delta\theta}{\theta_o} = -P_1^{-1}P - \frac{1}{2}P_2^{-2}P^2 \qquad (6)$$

where $\Delta\theta = (\theta - \theta_o)$ and θ_o is the value of θ at $P = 0$. If the influence of thermal expansion is neglected, the parameters are $P_1^{-1} \equiv \sum_j A_j$ and $P_2^{-2} = \sum_j \lambda_j^2 A_j^2$, which contain $\lambda_j \equiv \gamma_{uv}^j/\beta_{uv}^j$, $A_j \equiv \sum_i \beta_{uv}^j K_{ji}$, $B_j \equiv \sum_i \beta_{uv}^j K_{ji} \sum_k \alpha_k c_{ki}$. The remarkable susceptibility above T_c in Fe_2P indicates that

$$\theta = T_c\,(1 + a + p^{-1}P + \cdots) \quad \text{or} \quad \Delta\theta \approx (1 + a)\,\Delta T_c + T_c p^{-1} P \qquad (7)$$

So long as $\lambda_j^2 \Delta\theta/\theta_o \ll 1$ remains valid, substitution of eq. (7) into eq. (6) gives

$$P = -Q_1 \Delta T_c - Q_1^2 Q_2\,(\Delta T_c)^2 \qquad (8)$$

where $Q_1 \equiv (1 + a)\,[(\theta_o/P_1) + (T_c/p)]^{-1}$ and $Q_2 \equiv (\theta_o/2P_2^2)\,[(\theta_o/P_1) + (T_c/p)]^{-1}$. Comparison of eq. (8) with eqs. (1) and (2) shows that eq. (4) has the correct form and that $Q_1Q_2 \sim 3 \times 10^{-3}\ [K]^{-1} \sim \theta_o^{-1}$. Therefore $(P_1/P_2) \sim 1$, or $\lambda_j \sim 1$. If all the constants but θ_o and T_c in Q_1Q_2 are the same for Fe_2P and $Fe_2P_{0.9}As_{0.1}$, the ratio of the respective θ_o are $252 \times 1.7/710 \times 1.2 \approx 1/2$. The measured Curie temperatures at 1 atm are $T_c = 221K$ and $341K$, respectively, which demonstrates the essential self-consistency of the analysis. In fact, the small discrepancy can be qualitatively accounted for by the observation that the pressure sensitivity of T_c, and hence p, is larger in Fe_2P.

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