# 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 $\mu_o$ to 11 kbar. In $Fe_2P$, the relation between $\Delta T_c$ [° 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 $\mu$ 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 $\nu$-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 $\mu_A$ (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 $\mu_o$ 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 $\mu_o$ 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