Singlet Semiconductor to Ferromagnetic Metal Transition in FeSi

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Adding the local Coulomb repulsion to the local density approximation, the so-called LDA + U scheme, leads us to predict a first order transition from a singlet semiconductor to ferromagnetic metal in FeSi with increasing magnetic field. Extensions to finite temperature lead to the interpretation that the anomalous behavior at room temperature and zero field arises from proximity to the critical point of this transition. This critical point at a finite field may be accessible in currently available magnetic fields.

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FeSi displays an unusual crossover from a singlet semiconducting ground state with a narrow band gap to a metal with an enhanced spin susceptibility and a Curie-Weiss temperature dependence in the vicinity of room temperature [1]. Various models have been put forward to explain this behavior, starting with the very narrow band description of Jaccarino *et al.* [2]. Takahashi and Moriya [3] proposed a nearly ferromagnetic semiconductor model, predicting thermally induced spin fluctuations which were subsequently confirmed experimentally [4]. Recently, models based on treating FeSi as a transition metal analog of the Kondo insulators found in heavy-fermion–rare-earth systems have been much discussed [5,6].

Electronic structure calculations using a local density approximation (LDA) by Mattheiss and Hamann [7] correctly account for the narrow gap semiconducting ground state but more is required to explain the anomalous behavior. In this Letter we report calculations based on the LDA + U scheme, a generalization of the LDA method introduced by Anisimov *et al.* [8,9] to include the influence of local Coulomb interactions on the electronic structure and magnetic properties of real systems in the mean-field approximation. Our key result is the prediction of a first-order transition in an external magnetic field B to a metallic ferromagnet with a magnetic moment of $1\mu_B$/Fe. Using an approximate finite temperature generalization we find this singlet semiconductor to ferromagnetic metal transition line ends at a critical point (T_c, B_c) with T_c around room temperature. While we cannot predict B_c accurately, we are led to propose that the crossover observed in zero field arises through proximity to this critical point and that this critical point may be accessible in high field measurements.

The main idea of the LDA + U method is that the LDA gives a good approximation for the average Coulomb energy of d-d interactions, $E_{\rm av}$, as a function of the total number of d electrons, $N = \sum_{m\sigma} n_{m\sigma}$, where $n_{m\sigma}$ is the occupancy of a particular $d_{m\sigma}$ orbital

$$E_{\rm av} = \tfrac{1}{2} UN(N-1) - \frac{1}{4} JN(N-2). \qquad (1)$$

But LDA does not properly describe the full Coulomb and exchange interactions between d electrons in the same d shell. So Anisimov *et al.* [8,9] suggested to subtract $E_{\rm av}$ from the LDA total energy functional and to add orbital- and spin-dependent contributions to obtain the exact (in the mean-field approximation) formula

$$E = E_{\rm LDA} - E_{\rm av} + \frac{1}{2} \sum_{m,m',\sigma} U_{mm'} n_{m\sigma} n_{m'-\sigma} + \frac{1}{2} \sum_{m\neq m',m',\sigma} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma}. \qquad (2)$$

Taking the derivative with respect to $n_{m\sigma}$ gives the orbital-dependent one-electron potential

$$V_{m\sigma}(\vec{r}) = V_{\rm LDA}(\vec{r}) + \sum_{m'} (U_{mm'} - U_{\rm eff}) n_{m'-\sigma} + \sum_{m'\neq m} (U_{mm'} - J_{mm'} - U_{\rm eff}) n_{m\sigma} + U_{\rm eff}\left(\frac{1}{2} - n_{m\sigma}\right) - \frac{1}{4} J, \qquad (3)$$

with $U_{\rm eff} = U - \frac{1}{2} J$.

The Coulomb and exchange matrices $U_{mm'}$ and $J_{mm'}$ are expressed through the integrals over products of three spherical harmonics and screened Coulomb and exchange parameters U and J [8,9].

A nontrivial problem is what value of the screened Coulomb interaction U to use. For insulators such as late-transition-metal oxides a good approximation is to calculate static screening of the d-d intrashell Coulomb interaction in a supercell LDA calculation [10]. But if d electrons themselves are enough delocalized to take part in the screening, dynamical screening occurs—a difficult

problem that can be treated, e.g., in the *GW* approximation [11].

Dynamical screening is clearly essential for metallic systems, e.g., the statically screened U for Fe metal is $\approx$6 eV [9], which is certainly too large. The empirical values for U chosen to give an agreement with experiment in Fe lie between 1 and 2 eV [12]. FeSi is a semiconductor but with a very small band gap, so the value of U should lie between these extremes. (Note, if dynamical screening is explicitly included as in the exact solution for a finite cluster [13] then the value of U which gives agreement with experiment is quite large; $\gtrsim$4 eV.)

If we set $U = 0$, our method becomes equivalent to standard LDA. In Fig. 1(a) the density of states (DOS) obtained with $U = 0$ is shown. It is quite close to the results of previous LDA calculations [7]. The Stoner parameter I is not strong enough to produce a magnetic state and the only stable solution is nonmagnetic. As one increases U above the critical value $U_c = 3.2$ eV, a metastable magnetic solution appears with a moment per Fe site of $\mu = 1\mu_B$. The nonmagnetic solution is still present with a total energy $\approx$0.3 eV/Fe lower. For $U > 4.6$ eV the magnetic state is lower in energy and so becomes the ground state.

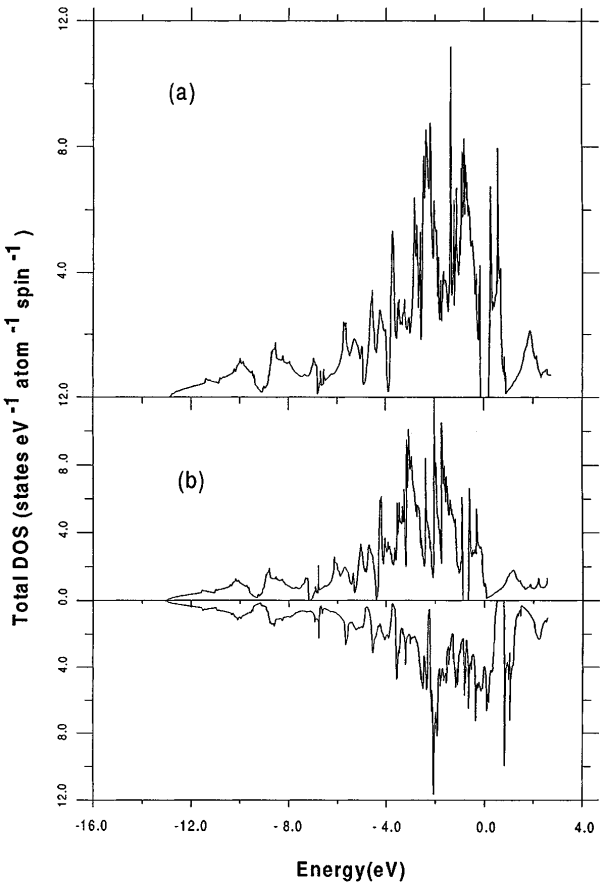

FIG. 1. Density of states (DOS) from LDA + U calculations. The Fermi energy, E_F, is the zero of energy. (a) Nonmagnetic state with $U = 0$; (b) majority and minority spin bands in a ferromagnetic state with a moment of $1\mu_B$/Fe.

We also performed so-called "fixed spin moment" calculations for the total energy, Eq. (2), as a function of the moment μ per Fe (Fig. 2). For $U < U_c$ there is only one local minimum corresponding to $\mu = 0$. Near $\mu \approx 1\mu_B$ there is only a bend in the curve but no minimum. For $U \gtrsim 3.4$ eV a second local minimum appears but it lies higher in energy. However, for $U =$ 5.4 eV, this minimum at $\mu \approx 1\mu_B$ is clearly lower than the nonmagnetic one.

On Fig. 1(b) the DOS of the magnetic solution with $U = 3.4$ eV is presented. One can see why $\mu \approx 1\mu_B$. The nonmagnetic DOS [Fig. 1(a)] has a peak just above the Fermi level, E_F, contains 2 electrons per spin per unit cell which is separated from the remaining higher energy states. In the magnetic solution [Fig. 1(b)] this peak is fully occupied for the majority spin giving a total moment of $4\mu_B$ per unit cell containing 4 Fe atoms.

In contrast to the transition metal oxides where the 3d bands are well separated from lower lying O 2p bands,

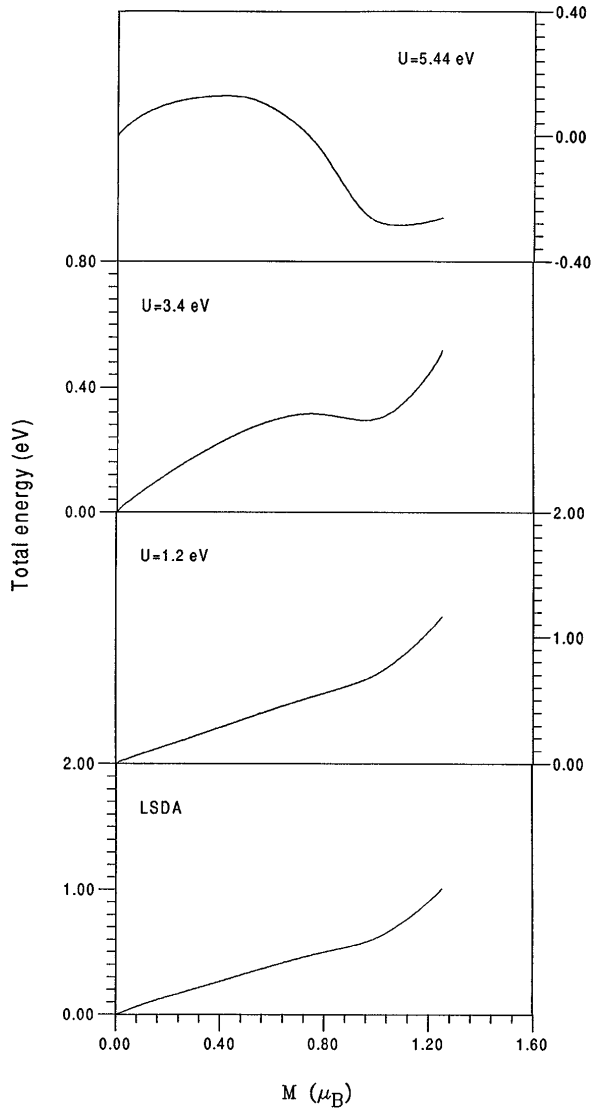

FIG. 2. Total energy as a function of the spin moment $\mu(\mu_B/\text{Fe})$ with various values of U.

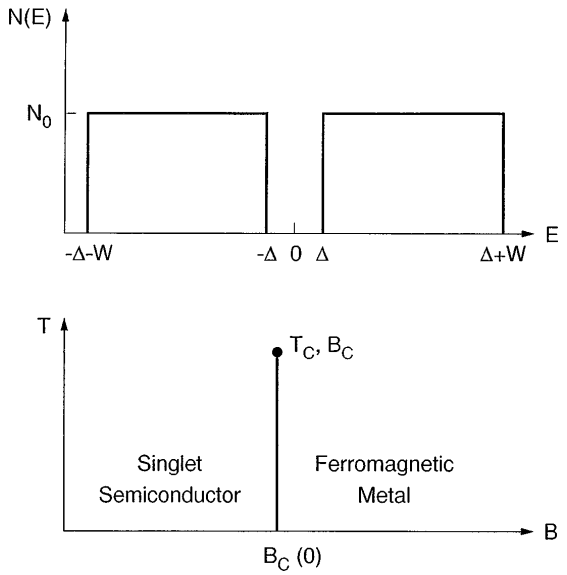

FIG. 3. (a) Density of states of the model band structure; (b) phase diagram in the (T,B) plane.

FeSi has very broad common Fe $3d$–Si $3p$ bands. So the formal valence and relevant d^n configuration of the Fe ion are not obvious. To resolve this question one has to look at the dispersion curves $\epsilon(k)$ (Fig. 2 and Fig. 3 in [7]). At the high-symmetry R point of the Brillouin zone the lowest levels are 4-degenerate Si 3s states at -9 eV, and 4-degenerate Si $3p$ states at -6 eV. Next come two 8-degenerate levels of Fe $3d$ origin below E_F at -3 eV and at -1 eV, respectively, and one 4-degenerate level also of Fe $3d$ origin just above E_F. The bands of Si $3p$–Fe $4s$,$4p$ origin all are higher in energy.

We suggest the following interpretation. Si $3s$ bands do not cross with other bands and are filled. Si $3p$ orbitals form occupied bonding and unoccupied antibonding bands (the latter are in the same manifold with Fe $4s$,$4p$ derived bands). The filled bonding Si $3p$ band contains 8 electrons per 4 Si atoms in a cell, that correspond to the neutral Si atom ($3s^2 3p^2$ and formal Si valence 0). The Fe atom is also neutral ($3d^8$ and formal valence 0). The point group symmetry of the Fe site is C_3 (Bravais lattice is cubic) and the $3d$ levels split into two 2-degenerate and one nondegenerate levels as seen at the R-point which has the total symmetry of the lattice. Crudely speaking, FeSi is a neutral Fe impurity in crystal Si (this analogy is not completely valid as Si $3p$ and Fe $3d$ bands are separated only near R and are strongly mixed elsewhere).

This interpretation disagrees with the Kondo-insulator hypothesis [5] which requires a local $3d$ level hybridizing with s,p levels at the Fermi energy. Instead a form of high spin–low spin transition in the $3d$ bands of the Fe ions is suggested, similar in spirit to the models of Ref. [3]. Note the high spin state with a moment of only $1\mu_B$/Fe is not compatible with a local ionic description but is a consequence of the band structure as discussed above.

The second local minimum in $E_g(\mu)$ leads to a first order transition in an external magnetic field. Although the moment ($\mu = 1\mu_B$/Fe) of the ferromagnet is insensitive, the critical field B_c of the transition is very sensitive to U; e.g., for $U = 3.4$ eV (see Fig. 2), B_c is very large ($\sim 10^3$ T), but for $U \geq 4.6$ eV, $B_c = 0$ and the magnetic solution is the most stable. It is not possible to make an accurate *a priori* estimate of B_c. Instead we resort to simpler models guided by the *a priori* calculations and adjust the model parameters to agree with the measured spin susceptibility $\chi(T)$ and specific heat $C_p(T)$.

We use a rectangular form (width W) for both the electron (conduction) and hole (valence) DOS separated by a gap 2Δ. Each band contains one state per Fe including spin. At finite temperature T and magnetic field B we use an approximate Landau form for the free energy.

$$F[T,B] = \sum_{\tau,\sigma} \int d\epsilon N(\epsilon)(\epsilon - g\mu_B B\sigma) n_{\tau,\sigma}(\epsilon) - \frac{1}{2} I\mu^2 - \frac{1}{2} V\rho^2 + T\sum_{\tau,\sigma} \int d\epsilon N(\epsilon)\{n_{\tau,\sigma}(\epsilon)\ln[n_{\tau,\sigma}(\epsilon)] + [1 - n_{\tau,\sigma}(\epsilon)]\ln[1 - n_{\tau,\sigma}(\epsilon)]\}. \quad (4)$$

The subscripts τ ($=e,h$) denote the bands and σ ($=\pm 1$) spin. The last term describes the interactions in terms of two Landau parameters I and V, associated with magnetization μ, and density of excited electrons and holes ρ,

$$\mu = \int d\epsilon\, N(\epsilon) \sum_{\tau} [n_{\tau,+}(\epsilon) - n_{\tau,-}(\epsilon)],$$
$$\rho = \int d\epsilon\, N(\epsilon) \sum_{\sigma} [n_{e,\sigma}(\epsilon) + n_{h,\sigma}(\epsilon)]. \quad (5)$$

If only the exchange interactions are included then $I = V$. In FeSi we expect $I \approx V$ but allow a small difference between I and V in our fitting procedure. F(T,B) is minimized with respect to the occupation numbers $n_{\tau,\sigma}(\epsilon)$ and (μ,ρ).

At $T = 0$, there is a first order transition with increasing B between a singlet semiconductor ($\mu = \rho = 0$) and a fully polarized state ($\mu = \rho = 1$) identical to the LDA + U calculations, at a value $B = B_c(0)$ given by

$$g\mu_B B_c(0) = \Delta + [1 - 2N_0(I + V)]/4N_0. \quad (6)$$

The line of first order transitions at $T > 0$ ends in a critical point (T_c, B_c). We calculated $\chi(T)$, and the electronic entropy $S(T)$ (second term in Eq. (4)) and $Cp(T)$ and adjusted the parameters (I, V, Δ, and W) to

fit the data at $B = 0$ by Jaccarino *et al.* [2], as shown in Figs. 4 and 5. Reasonable fits require small values of $B_c(T)$ so that the critical point is near the specific heat peak at $B = 0$. The parameters $I = 0.07$ eV and $V = 0.075$ eV, together with $g = 2$ and a narrower bandwidth W (=1/8 eV) and band gap ($2\Delta = 40$ meV) than in the LDA band structure lead to $B_c(0) = 170$ T. The line of first order transitions [Fig. 3(b)] is essentially at constant B and ends at a critical point ($T_c = 280$ K, $B_c = 170$ T). Note in the real band structure the ferromagnetic state is metallic leading to a semiconductor-metal transition at constant B with increasing T thereby lowering B_c.

The fits to $\chi(T)$ and $Cp(T)$ are reasonable. Note, Jaccarino *et al.* [2] achieved a better fit to $\chi(T)$ with a simple 2-level model, but used an arbitrary g factor of $g = 3.92$ (not $g = 2$) roughly equivalent to a strong exchange enhancement ($\sim$4). Similarly the fits with model bandstructures similar to Fig. 3(a) by Mandrus *et al.* and Sales *et al.* [6] include enhancements $\sim$4. Our fits offer a new interpretation of the anomalous $\chi(T)$ and $C_p(T)$ in FeSi. The proximity to a critical point of a semiconductor to metal transition in the (T, B) plane is the origin of the anomalous behavior. Alternatively, even at $B = 0$ there is a strong renormalization of the band gap due to the attraction between thermally excited electrons and holes leading to a crossover to an exchange enhanced metallic state.

In conclusion, LDA + U calculations predict a first order low spin–high spin transition from a singlet semiconductor to a metallic ferromagnet in FeSi in a strong magnetic field. The critical point may be accessible in magnetic fields $\sim$100 T and experiments would be most welcome.

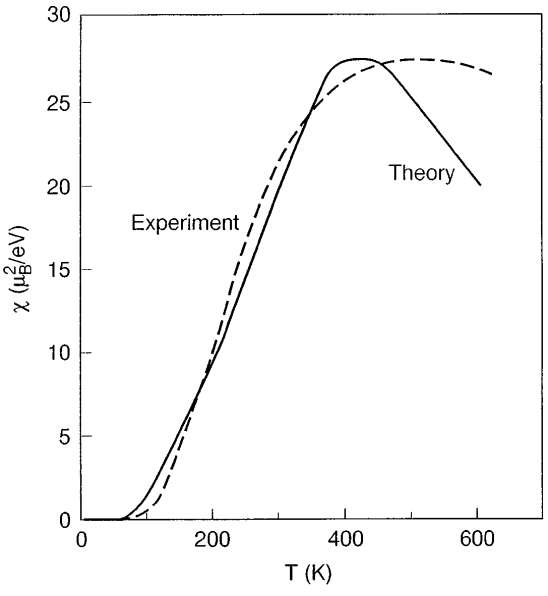

FIG. 4. Spin susceptibility $\chi(T)$ from this calculation and from experiment (Ref. [2]).

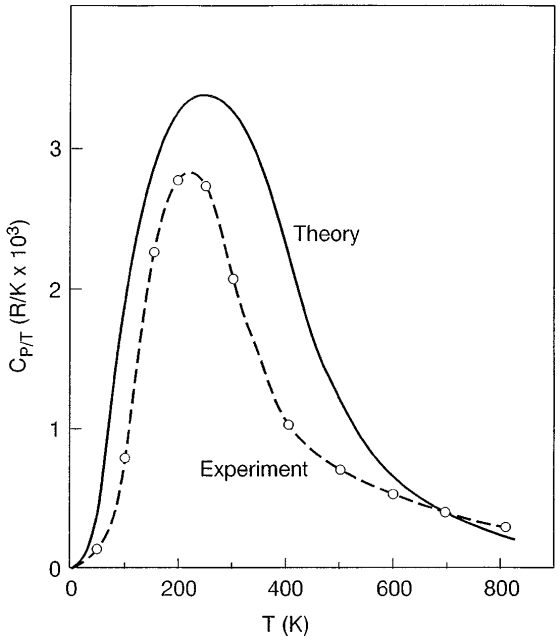

FIG. 5. The electronic part of the specific heat, $Cp(T)$ plotted as Cp/T vs T. Experimental data points are from Ref. [2].

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