Ferromagnetism of Ga$_{1-x}$Mn$_x$As and Weiss theory of Curie temperature in the coherent potential approximation

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The zinc-blende GaAs-based III-V diluted magnetic semiconductors (DMS) are studied in the coherent potential approximation (CPA). In this work, we use the exact Hilbert transformation of the face-centered cubic (fcc) density of states (DOS), which is different from the usual semi-circle density of states employed in our previous work. Our calculated relation of ground-state energy and impurity magnetization shows that ferromagnetism is always favorable at low temperatures. For very weak Kondo coupling, the density of states (DOS) of the host semiconductor is modified slightly. Impurity band can be generated at the host band bottom only when Kondo coupling is strong enough. Using Weiss molecular theory, we predict a nonlinear relation of Curie temperature with respect to Kondo coupling, as is different from the conclusion of our previous calculations based on semicircle DOS. The agreement of our calculated $T_C$ with measured values is convincing.

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The ferromagnetism of DMS of III-V-type is not well understood. To explain ferromagnetism in DMS, various models and approaches have been proposed. Though the models differ from each other in details, they all agree that the coupling between the carriers and local spins is of fundamental importance. An issue of debate, however, is how the exchange between localized spins is induced by the carriers. One model for this induced exchange is the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. Another version which results in conclusion equivalent to RKKY is the Zener model which uses the fact that the valence holes are on p-orbitals. A third model is the double-exchange (DE) mechanism. But this model is inconsistent with the charge-transfer properties. Though RKKY can give a Curie temperature in agreement with experiment, some argue that the RKKY model breaks down here because the local coupling between the carrier and the impurity spin is much larger than the Fermi energy and can not be treated perturbatively. In dealing with the effect of the localized spins, a key issue is whether or not randomness should be taken into consideration. The above models are all mean field approximations (MFA) which assume homogeneity and neglect randomness. But DMSs are disordered systems with positional disorder of Mn impurities. As concluded in, disorder has a substantial influence upon carrier magnetic susceptibility. Hence, any first principle consideration should take into account the randomness of the impurities.

A classic method of dealing with randomness is the coherent potential approximation (CPA) which has been applied to DMS. Basing on the formalism of CPA and assuming very large local spin $S$ while keeping the product $JS$ constant (where $J$ is the Kondo -like interaction), detected the density of states and the relation between Curie temperature and the doping concentration. Using the averaged carrier Green’s function, arrived at the conclusion that the local coupling between the carrier and the impurity spins must be intermediate in order to acquire ferromagnetism. In our previous work, we used the formalism of CPA to study the ground-state properties of III-V DMS. The DOS for the undoped crystal we used is the semicircle DOS. In contrast to, we kept $S = 5/2$ and treated the impurity spins fully quantum mechanically. Though it is mostly accepted that in III-V type DMS the effective spin of valence holes is $3/2$ and not $1/2$ fermions. It is usually believed that such a description can still catch the essential physics. Because of spin-orbit interaction, the p-orbitals are split (with split-off $\geq 0.34eV$) into a spin-3/2 multiplet and a spin-1/2 multiplet. Using spherical approximation, the kinetic energy of the Luttinger-Kohn Hamiltonian for the spin-3/2 multiplet takes the form

$$\sum_{\mu}(h^2k^2/2m_{\mu})c_{\mu}^\dagger c_{\mu},$$

near the valence top after diagonalization, where $m_{\mu} = m_h \approx 0.5m$ for $\mu = 3/2$ and $m_{\mu} = m_{\ell} \approx 0.07m$ for $\mu = 1/2$ ($m$ is the effective mass of a free hole). The interaction between the spin of holes and local 5/2-spins now takes a k-dependent form

$$\sum_{i,k,k'}S_i^z c_{i,k'}^\dagger J(k,k')c_{i,k} \exp(-i(k-k').R_i)$$

Since the DOS for parabolic band is $g(\epsilon) = (1/2\pi^2 h^2)(2m)^{3/2}/\sqrt{\epsilon}$, we have the ratio of DOS $g_h(\epsilon)/g_l(\epsilon) \approx 19$ for heavy holes and light holes, i.e., most of valence holes are heavy holes. Therefore, it is a valid approximation to consider only heavy holes. Moreover, since the hole density is very small, the Fermi wave vector is supposed to be very small and the it is thus a reasonable approximation to consider $J(k,k') \approx J(0,0)$ in the interaction term.

And this leads to the usual assumption that the carriers are shallow holes and the coupling of the shallow holes to the Mn$^{2+}$ can be described by local Kondo interaction between 5/2-spins and 1/2-spins. The system
is highly compensated \(^{26}-^{25}\) and the carriers are holes originating from randomly distributed Mn. There are different kinds of randomness, e.g., substitutional randomness, interstitial randomness, antisite randomness, and directional randomness of impurity spins. It is commonly agreed now that interstitial Mn atoms and antisite As only reduce the hole densities and do not affect conduction of holes significantly. Therefore we consider only two kinds of randomness, i.e., the random substitution of the Mn atoms and the random direction of the impurity spins.

Since the DOS for undoped crystal is much involved in the CPA calculations and the real structure of Ga\(_{1-x}\)Mn\(_x\)As, where the doping concentration \(x\) varies from 0.015 to 0.08 in region of interest for ferromagnetism \(^{26}\), is of zinc-blende structure, we here use the method developed in our previous work to study DMS Ga\(_{1-x}\)Mn\(_x\)As, taking into consideration the real fcc lattice structure. In as-grown samples of \(^{26}\), ferromagnetism was realized at Curie temperature of 76K at \(x = 0.05\). The hole density \(p\) varies from 5.6%\(x\) \(\sim\) 93%\(x\). We use the tight-binding model Hamiltonian

\[ H = \sum_{i,j,\sigma} t_{ij} \sigma_i \sigma_j + \sum_{i} u_i \]  

(1)

where \(u_i\) depends on whether \(i\) is a Ga or Mn site. For Ga-site \(u_i = u_i^G = E_G \sigma_i \sigma_j + J_{K} \sigma_i \sigma_j\), and for Mn-site \(u_i = u_i^M = E_M \sigma_i \sigma_j + J_{K} \sigma_i \sigma_j\), \(s_i\) is the local spin of Mn at site \(i\), \(\sigma = (1/2) \sigma_i \sigma_j \sigma\) is the spin of a hole where \(c_i\) is the creation(annihilation) operators for holes, \(\sigma\) spin indices \(\sigma = \uparrow, \downarrow\), and \(\tau = (\tau_1, \tau_2, \tau_3)\) are the three usual Pauli matrices. \(E_M\) and \(E_G\) are the on-site energies for Ga and Mn and are assumed constant. The hopping energy \(t_{ij} = t\) if \(i, j\) are nearest neighbors and zero otherwise and \(J_K > 0\) is the local Kondo coupling. According to the general scheme of CPA, the virtual unperturbed Hamiltonian is

\[ \mathcal{H}(\varepsilon) = \sum_{\sigma,k} (E_k + \Sigma(\varepsilon)) c_{\sigma k}^\dagger c_{\sigma k} \]  

(2)

where \(\varepsilon\) is the Fourier frequency variable, \(\Sigma(\varepsilon)\) is the CPA self-energy to be determined self-consistently and \(E_k\) is the Fourier transformation of \(t_{ij}\). Then the relative perturbation \(V\) is given by

\[ V = H - \mathcal{H}(\varepsilon) = \sum_{i} v_i \]  

(3)

where \(v_i = v_i^G = \sum_{\sigma}(E_G - \Sigma(\varepsilon)) c_{\sigma i}^\dagger c_{\sigma i}\) for Ga and \(v_i = v_i^M = \sum_{\sigma}(E_M - \Sigma(\varepsilon)) c_{\sigma i}^\dagger c_{\sigma i} + J_K \sigma_i \sigma_j s_i\) for Mn. The reference Green’s function is \((\Sigma|\mathcal{H}(\varepsilon)|\Sigma) = \langle 0 | c_{\sigma i} \varepsilon - \mathcal{H} - 1 | c_{\sigma i}^\dagger \rangle\) where \(0\) is the vacuum state of the c-operators, and the associated t-matrices are \(t_i^G = v_i^G/(1 - \mathcal{H}V(1)^G)\), \(t_i^M = v_i^M/(1 - \mathcal{H}V(1)^M)\). So the CPA equation and DOS are given by

\[ (1 - x) t_i^G + x (t_i^M)_{\text{spin}} = 0 \]  

(4)

and

\[ g_\sigma(\varepsilon) = -\frac{1}{\pi} \text{Im} F_\sigma(\varepsilon) \]  

(5)

where \((\cdots)_{\text{spin}}\) denotes average over the configurations of impurity spins and \(F_\sigma(\varepsilon)\) is the Hilbert transformation of DOS, \(F_\sigma(\varepsilon) = \langle \sigma|\mathcal{H}|\sigma\rangle = (1/N) \sum_k [1/(\varepsilon - E_k - \Sigma(\varepsilon))]\) where \(N\) is the number of lattice sites. For any \(f(S^z)\), the spin average is given by \((f(S^z))_{\text{spin}} = \sum_{S^z} \langle S^z \rangle f(S^z) / \sum_{S^z} \langle S^z \rangle e^{\lambda S^z}\) where \(\lambda\) is determined by the condition \((S^z)_{\text{spin}} = m\) is the given magnetization of the impurity spins. In our single-particle CPA, the Callen-Shtrikman relation \(^{27}\) that tells there is a one-to-one correspondence between \(m\) and \((\langle S^z \rangle)_{\text{spin}}\) for \(n > 1\) applies. These explicit forms of CPA equations \(^{4}\) are given by \(^{10}\) in another context. To solve CPA equations, we need to know \(F_\sigma(\varepsilon)\). Jelitto \(^{28}\) and Iwata \(^{29}\) first gave a rigorous calculation of the \(k\)-integrated Green’s function for fcc tight-binding Hamiltonian. The expression entails complete elliptic integral and the analytic properties are very complicated. Morita \(^{30}\) et al made further discussions later. A much improved expression of the \(k\)-integrated Green’s function is obtained quite recently \(^{31}\). In unit of \(w/4\) where \(w\) is the band width and defining

\[ \kappa(\varepsilon) = \frac{1}{2} [1 - 4\sqrt{-\varepsilon \varepsilon - (1 + \varepsilon) \varepsilon - (1 - \varepsilon) \varepsilon - 3 - \varepsilon}] \]  

(6)

then \(F(\varepsilon)\) can be written as

\[ F(\varepsilon) = \frac{4}{\pi^2 (1 - \varepsilon)^{3/2}} (\sqrt{-\varepsilon - 3 - 2\sqrt{-\varepsilon}}) K^2(\kappa) \]  

(7)

where \(K(\kappa)\) is the complete elliptic integral

\[ K(\kappa) = \int_0^{\pi/2} d\theta \frac{1}{\sqrt{1 - \kappa \sin^2 \theta}} \]  

(8)

At zero temperature, the carrier density for spin \(\sigma\) can be expressed as \(n_\sigma = \int_{-\infty}^{\infty} g_\sigma(\varepsilon) d\varepsilon\) where \(\varepsilon_F\) is the Fermi energy, and the total carrier density \(n = n_\uparrow + n_\downarrow\). The total electronic ground-state energy per site is \(\varepsilon_g = \int_{-\infty}^{\infty} \varepsilon [g_\uparrow(\varepsilon) + g_\downarrow(\varepsilon)] d\varepsilon\).

In our numerical calculation, we chose \(w = 4.0\) eV which is roughly the bandwidth of the heavy holes \(^{32}\) and set \(E_G = 0\) since we can shift the chemical potential without loss of physics. (Note that the effective mass for tight-binding spectrum is related to the bandwidth by \(m_h = 8h^2/(\omega a^2)\) where \(a \approx 5.6532\)Å. This relation gives \(m_h \approx 0.48m_e\) for \(w = 4\) eV). FIG. \(1\) shows DOS for some given model parameters. The corresponding hole density is \(p \approx 0.442\) for as-grown samples as provided in \(^{26}\). The left panel shows DOS in the full range for some given model parameters; the right panel is an enlarged display for the range \(-4\) to \(-2\). As a check for our numerical results, the sum rule \(\int_{-\infty}^{\infty} g_\sigma(\varepsilon) d\varepsilon = 1\) and
FIG. 1: Left panel: DOS in the full range for some given model parameters; Right panel: enlarged display from $\varepsilon = -4$ to $\varepsilon = -2$, the Fermi energies are for as-grown samples from [24]

FIG. 2: Relation of $\varepsilon_n$ versus $m$. B: $J_K = 0.6$; C: $J_K = 0.8$; D: $J_K = 1.0$; E: $J_K = 1.2$; F: $J_K = 1.4$; G: $J_K = 1.6$; H: $J_K = 1.8$. $x = 0.05$, $p = 0.442x$, $w/4 = 1.0$ eV

the relation $n_\uparrow + n_\downarrow = p$ are also preserved where $n_\sigma$ is calculated from spin-resolved DOS respectively. As can be seen that for $J_K = 1.2$, there is no separate impurity band and the DOS is not substantially different from the bare DOS in shape. When Kondo coupling $J_K = 1.8$, separate impurity bands show up. Fig.1 also shows that for $m > 0$, there are always more spin-down carriers than spin-up carriers, in compliance with the fact that the local $p$-$d$ coupling is antiferromagnetic [4].

FIG. 3 shows the relation between ground-state energy per site and the impurity magnetization $m$. In actual calculation of ground-state energy, an important issue is the determination of the Fermi energy which is fixed by the integration of an interpolation function of the DOS. If the interval $\delta \varepsilon$ is not small enough, the integral of the interpolated DOS may vary significantly with the choice of $\delta \varepsilon$. To make it stable enough, we choose $\delta \varepsilon = 5 \times 10^{-4}$ to interpolate DOS linearly. Our results show that for all the chosen values of model parameters, the ground-state energy per site always decreases, though very slowly, with increase of impurity magnetization. Therefore CPA predicts that at very low temperatures, ferromagnetism is always energetically favorable for all the model parameters considered.

In FIG. 3, we show the dependence of Curie temperature on the model parameters and the doping concentration. As proposed in our previous work [13], Weiss molecular field theory can be employed to calculate the Curie temperature. Given $m$, one can calculate DOS and then $\langle s_z \rangle$. So one can establish relation $\langle s_z \rangle = \langle s_z \rangle(m)$. On the other hand, given $\langle s_z \rangle$, each impurity spin feels an effective field $J_K \langle s_z \rangle$ and thus we have $m = S B_S(\beta h)$ with $h = -J_K \langle s_z \rangle(m)$, $\beta = 1/k_B T$ and $B_S(x)$ the conventional Brillouin function. For very small $m$, we have $\langle s_z \rangle \simeq -Am$ with $A > 0$ and we have $\beta h \simeq \beta J_K Am$. So $B_S(\beta h) \simeq (S + 1)\beta h / 3$ and thus the Curie temperature can be estimated by $k_B T_C \simeq J_K S(S + 1)A / 3$. For small $m$, letting $F_1(z) = F(z) + \psi(z)m$, $F_2(z) = F(z) - \psi(z)m$ where $F(z)$ is the paramagnetic solution, we have

$$A(J_K, E_M, x, \beta) \simeq \frac{1}{\pi} \int_{-\infty}^{+\infty} d\varepsilon \Im \psi(\varepsilon)$$

where we have ignored the $\beta$-dependence. As our numerical results (not shown here) indicate, the chemical
potential is very close to the zero temperature Fermi energy in a wide range of temperatures ($\beta > 50$), showing that the Fermi function can be approximated by the zero temperature step function. The left panel in FIG.3 shows the relation of $T_C$ versus $J_K$ for different values of $E_M$. Unlike the result from semicircle DOS [15], the curves exhibit a nonlinear relation. The right panel shows the dependence of Curie temperature on the doping concentration for $J_K = 2.03$, $E_M = 0$ and $J_K = 1.2$, $E_M = -3.25$ for the as-grown samples in [26]. These two sets of parameters are chosen so that at $x = 0.05$, $T_C = 76$ K. It is seen that our CPA+Weiss approach for $T_C$ does reveal the observed behavior. Our result show that both sets of values $J_K$, $E_M$ can explain the measured results.

To conclude, we summarize our results here. Using CPA and treating the impurity spins fully quantum mechanically, we have calculated the ground-state energies of GaAs-based III-V DMS for a wide range of model parameters. The results show that ferromagnetism is always preferable at low temperatures. With the help of Weiss molecular theory of ferromagnetism, we obtained a nonlinear relation of Curie temperature with respect to Kondo coupling. Our theoretical prediction of relation $T_C \sim x$ does fit quite well the measured results for as-grown samples [26]. The deviations of our calculated results from the experimental values is due to the sensitivity of $T_C$ to the hole density or the ratio $p/x$, which is difficult to be measured precisely. Though the value of $J_K = 1.2$ eV is more generally accepted than other values, the actual value of $J_K$ is still an issue of debate. Our calculation allows adjustment of model parameters $J_K$, $E_M$ and the main features of numerical results for different model parameter values remain similar. Finally, a number of complicated models with complicated approximations have been proposed to calculate Curie temperatures (e.g. [28]). Yet, we believe that CPA, a method having been tested for decades, is still an effective way to understand ferromagnetism in DMS.

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