Ab initio description of the diluted magnetic semiconductor $Ga_{1-x}Mn_xAs$: Ferromagnetism, electronic structure, and optical response

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Motivated by a study of various experiments describing the electronic and magnetic properties of the diluted magnetic semiconductor $Ga_{1-x}Mn_xAs$, we investigate its physical response in detail using a combination of first-principles band structure with methods based on dynamical mean field theory to incorporate strong, dynamical correlations, *and* intrinsic as well as extrinsic disorder in one single theoretical picture. We show how ferromagnetism is driven by double exchange (DE), in agreement with very recent observations, along with a good quantitative description of the details of the electronic structure, as probed by scanning tunneling microscopy and optical conductivity. Our results show how ferromagnetism can be driven by DE even in diluted magnetic semiconductors with small carrier concentration.

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Spintronics is a rapidly emerging technology where it is not the electron charge but the electron spin that carries information. It offers promising opportunities for developing a new generation of devices based on a combination of standard microelectronics with spin-dependent effects arising from the interaction of the carrier spin with the magnetism of the material.[1] Another promising area envisions its marriage with optical photons, with the possibility of designing new spin based devices such as spin-field effect transistors (FET's), spin-light emitting diodes (LED's), optical switches operating in the THz range, modulators, encoders, and decoders, and bits for quantum computation.[2] Discovery of optically induced ferromagnetism in some Mn-doped III-V semiconductors opens up the possibility of applications to photonic storage devices and photonically driven micromechanical elements.[1] Success of this vision demands a deeper understanding of fundamental spin interactions in the solid state, along with the realistic bandstructures, and roles of dimensionality as well as intrinsic (extrinsic) defects.

The discovery of dilute magnetic semiconductors (DMS's), which are III-V semiconductors randomly doped with small amounts of magnetic atoms, such as Mn^{2+}, has provided us with an attractive example of prototype materials of great interest in this context.[3] These have ferromagnetic transition temperatures much higher than those of earlier known Eu-chalcogenides,[3] of order 100 K, and the magnetism can be controlled electronically. The optimum value of x in $Ga_{1-x}Mn_xAs$ corresponding to highest $T_c = 110$ K is $0.043-0.05$. In spite of much activity, the nature of ferromagnetism, as well as the detailed electronic structure, is not properly understood. Ultimately, the mechanism of FM should go hand-in-hand with the details of spin interactions in a system of dilute Mn^{2+} ions doped randomly in the GaAs host, and to the details of modification of the electronic structure due to Mn doping.

Application of the Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism provides some understanding of magnetic and transport properties of DMS's,[4] but is somewhat questionable in this case, since it is only valid when the exchange interaction, $J \ll E_F$, the Fermi energy of the carriers. This is obviously not the case in DMS's, where the carrier concentration is low.[5] An alternative double-exchange (DE) model based approach[5] has recently been invoked within a model band structure to study the evolution of T_c with x. However, the specific conditions under which DE ideas can be applied to DMS remain to be elucidated.

GaAs is a well known band semiconductor. Its electronic structure, however, is sensitive to As antisites forming in the bulk during growth. The importance of these defects in the GaAs host, constituting a source of *intrinsic* disorder, will become clear below. Each Mn ion in GaAs serves a dual purpose, acting as an acceptor as well as a magnetic impurity. In reality, the situation is a bit more complex when the realistic local characteristics of the Mn ion, such as the charge transfer energy ($E_{\mathrm{Mn}}-E_{\mathrm{As}}$), and the p-d hybridization (As−Mn), and Coulomb interactions, are taken into account. The importance of including such quantum chemical aspects is shown very clearly in spectroscopic measurements;[6] these yield the on-site Hubbard $U = 3.5$ eV, the charge transfer energy $\Delta = -1.5$ eV, and the hybridization $t_{pd} = 1.1$ eV. Additionally, the Hund's rule coupling $J_H \simeq 0.55$ eV, acting similar to a magnetic impurity potential.[5] Finally, the random distribution of the Mn ions gives rise to an additional non-magnetic disorder component. All previous theoretical works done for $Ga_{1-x}Mn_xAs$ have focused either on pure bandstructure aspects,[7] with the use of the coherent-potential-approximation (CPA) for treating Mn doping induced (magnetic+non-magnetic) disorder, or on model approaches,[5] and we are not aware of calculations which incorporate the strong correlation at Mn sites, along with local quantum chemical information (t_{pd}, Δ) and *intrinsic* As antisite disorder as well as Mn-doping related magnetic and nonmagnetic disorder into the complex band structure of this material in a consistent way. In addition, the LDA+CPA work[8] shows the As antisite band *above* the region of the DOS where half-metallicity is observed, in clear disagreement with the results of the STM measurement.[9] In addition, no study of optical response has been performed to date with such approaches. Very recent theoretical advances[10] have opened an attractive possibility to study the

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correlated bandstructure of materials involving transition metal oxides and rare-earth based compounds via local density approximation with dynamical mean field theory (LDA +DMFT).

In what follows, we show how a consistent theoretical (via LDA+DMFT) implementation including real band structures of GaAs, quantum chemical and strong correlation aspects mentioned above, and As antisite disorder is indeed necessary for a detailed quantitative understanding of the physics of $Ga_{1-x}Mn_xAs$.

A beautiful recent time-resolved magneto-optic measurement clearly shows the half-metallic character of the ferromagnetic metallic state in $Ga_{1-x}Mn_xAs$.[11] But this is not all, as the correlated nature of this state is further revealed by various responses. First, photoemission measurements[12] reveal very small spectral weight near the Fermi surface, and a T-dependent build-up of spectral weight at higher energies. Further, the change of the chemical potential E_F with Mn doping is intriguing. At small x, it appears to be almost pinned to its $x=0$ value, but starts moving towards the valence band (VB) around the x value where the semiconductor-metal transition accompanied by FM occurs. At $x>0.05$, it moves up again, concomitant with occurrence of insulating behavior with reduction of T_c, clearly showing the intimate connection between changes in electronic structure and variation in T_c as a function of x. More anomalous features are observed in optical measurements:[13] there is no quasicoherent Drude response; instead, the spectrum exhibits a peak centered around 1200 cm^{-1}, with a curious bump at lower energies. From a ''modified Drude fit,'' an effective mass $m^*=0.72m$ is deduced, in contrast to $m_b=0.24m$ from LDA calculations. The depression of the low-energy incoherent spectral weight with increasing T (decreasing magnetization) is also very clearly seen; what is interesting is that this spectral weight transfer (SWT) takes place over a wide energy scale of about 4 eV (much larger than T_c). These observations are inexplicable within bandstructure ideas, and constitute direct evidence for the importance of dynamical electronic correlations in $Ga_{1-x}Mn_xAs$.

While it provides a good description of ground state properties, the local density approximation (LDA) cannot describe the excited states of correlated systems, since the dynamical correlations in a *quantum* many-body system are neglected in the LDA. Thus, given the above arguments, a realistic description of $Ga_{1-x}Mn_xAs$ requires combining the LDA, which provides an excellent *ab initio* one-electron bandstructure of weakly correlated metals and band insulators,[7] with well controlled, state-of-the-art many body calculations capable of accessing the dynamical effects of strong electron correlations in a proper way. Recently, the combination of LDA with dynamical mean field theory (DMFT) has been shown to provide good quantitative description for various correlated systems.[10] Using LDA +DMFT, we will show how good quantitative agreement with DE ferromagnetism, STM data, and optical conductivity is obtained.

Local atomiclike features of Mn^{2+} in GaAs are obtained from the set of many-body levels describing processes of electron addition and/or removal in the atomic d shell. The

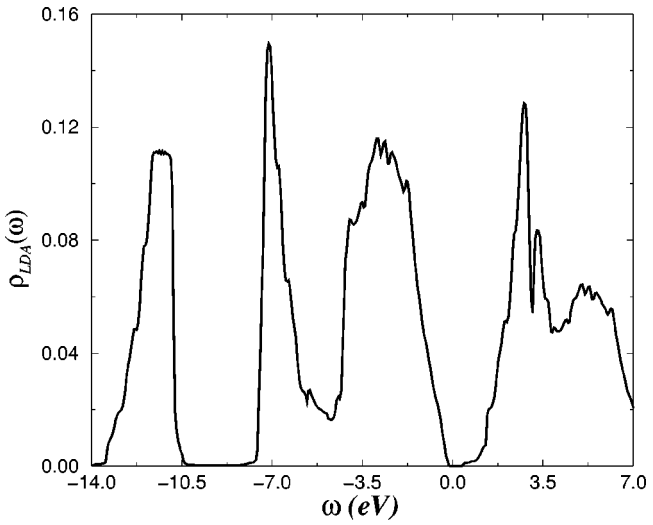

FIG. 1. Total density of states (DOS) of pure (without antisites) GaAs computed within the Kohn-Sham local density approximation (Ref. 7). The Fermi level is located at $\omega=0.0$.

constants U, J_H can be computed from first principles. Itinerant aspects of the actual solid enter via a dynamical bath function describing p-d hybridization; it quantifies the degree of itinerance of the d electrons, and needs to be determined in a self-consistent way from the DMFT equations. With this, the problem is reduced to solving an (asymmetric, in general) multiorbital Anderson impurity problem self-consistently embedded in a dynamical bath, giving us the impurity Green's function $G_{\rm imp}(\omega)$ and the self-energy $\Sigma(\omega)$.

The bands of GaAs are obtained from the eigenvalues of the matrix one-electron Hamiltonian $H(k)$, obtained from the LDA Kohn-Sham Hamiltonian.[7] The actual LDA density of states (DOS) for GaAs (without antisites) is shown in Fig. 1. In addition to a term describing the LDA band structure, the total Hamiltonian we will work with contains the Hubbard, hybridization, and charge transfer energy terms along with the term describing the local (As p-Mn d) Kondo coupling, with the parameter values chosen as given before. These were obtained from a cluster model analysis of the high-energy spectroscopic data, as in Ref. 6. They are not arbitrarily chosen free parameters, but are a faithful reflection of the local quantum chemistry of the Mn environment in GaAs.

To begin with, we model the effect of the random As antisite potential in pure GaAs using the usual coherent potential approximation (CPA).[14] Next, given the small concentration of Mn sites, we first solve the asymmetric Anderson impurity problem in the dynamical bath provided by the GaAs band structure for a single Mn impurity with the parameters given earlier, using the generalization of the iterated perturbation theory (IPT) for arbitrary filling.[10] The exact low-frequency behavior is obtained from the Friedel-Luttinger sum rule,[10] while the correct high-frequency behavior is obtained from a self-consistent computation of moments. These equations have appeared previously in various contexts,[10] and we do not reproduce them here. For the one-band Hubbard model, very good agreement with quantum Monte Carlo data has been reported at high T. For a concen-

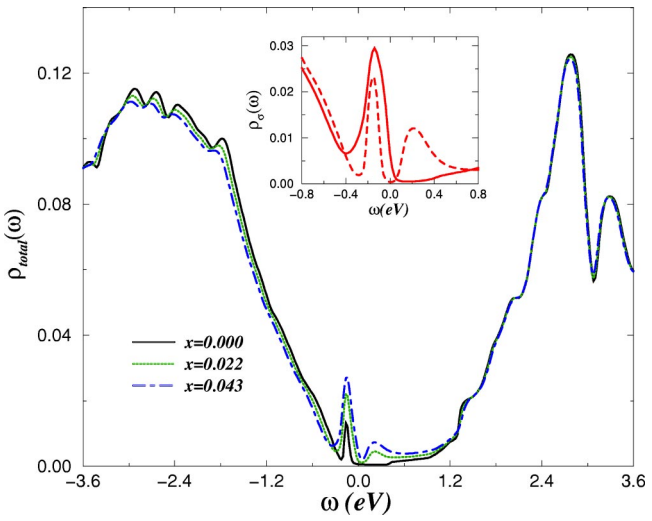

FIG. 2. (Color online) Renormalized total DOS of $Ga_{1-x}Mn_xAs$ as a function of x. For $x=0$, the additional impurity feature at $\omega=-0.1$ is related to the antisite ($n_{As}=0.015$) contribution (solid line). For $x=0.022$, a second Mn-doping related peak is resolved, but the system remains insulating (dotted line). With $x=0.043$ (dot-dashed), half-metallic behavior is clearly seen in the inset (bold and dashed lines correspond to majority- and minority-spin DOS), corresponding to DE ferromagnetism. Notice the good agreement with STM data (Ref. 9).

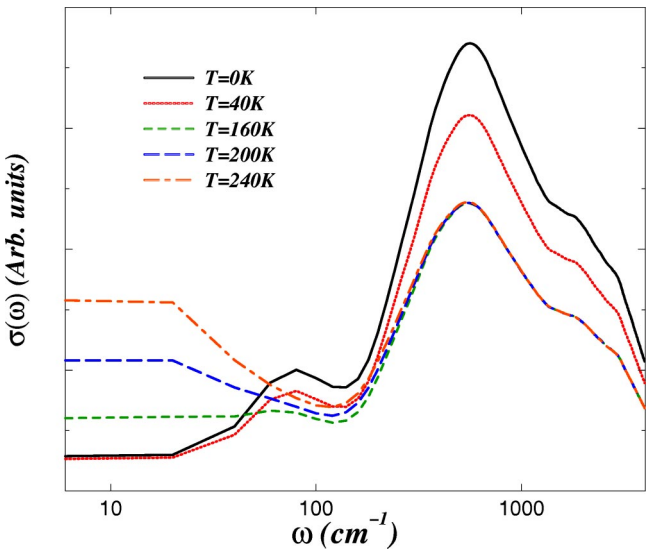

FIG. 3. (Color online) Computed optical conductivity $\sigma(\omega,T)$ versus ω for various T both below *and* above $T_c=120$ K. Good quantitative agreement with experiment (Ref. 13) is clearly visible.

tration x of Mn impurities, one has additionally to perform a configurational average over random Mn positions (nonmagnetic) as well as an average over all spin configurations of the Mn ions (magnetic). These effects of strong magnetic and positional disorder scattering are treated using the extended dynamical coherent potential approximation (CPA),[5] which is combined with IPT for the Mn impurities in a consistent way.[15]

Marriage of LDA with DMFT gives us a quantitative description of *both* ground- and excited-state properties. Finite temperature, and local moment effects above T_c are readily handled using temperature Green's functions within DMFT.

We now describe our results. In Fig. 2, we show the total density of states (DOS) for $Ga_{1-x}Mn_xAs$ for $x=0,0.022,0.043$ for our chosen parameter set. Given[9] that each Mn dopant creates an additional As antisite, the concentration of antisites, $n_{As}=0.015+x$. For $x=0$, the effect of the random As antisite disorder is modeled using CPA, resulting in an impurity (As) band of antisites split off from the VB in the semiconducting gap of GaAs. We draw attention to the good agreement of the calculated ($x=0$) DOS with STM data,[9] as well as to the fact that earlier LDA(+CPA) calculations predicted the antisite band to lie close to the bottom of the conduction band,[8] in direct conflict with STM results. For small $x=0.022$, the total DOS still indicates semiconducting behavior, in coincidence with conclusions from Ref. 16. Notice, however, the appearance of a second, broader peak in the gap. Again, this is in accordance with results of STM measurements.[9] Without random magnetic and nonmagnetic impurity scattering, a quasicoherent peak is obtained (not shown). Inclusion of strong magnetic (J_H) and positional disorder scattering by CPA washes out this low-energy coherence, resulting in the inset curve in Fig. 2. For $x=0.043$, metallic behavior, together with ferromagnetism (see below), is clearly revealed in the results (Fig. 2, dot dashed). Our results are very different from those of Korzhavyi *et al.*[8] and reproduce the STM observations very faithfully. From the real part of the one particle self-energy (not shown), we find $\partial\Sigma'(\omega)/\partial\omega|_{\omega=\mu}=-2.03$, leading to a mass enhancement of $m^*/m_b=3.03$ (here, m_b is the carrier mass estimated from LDA), in excellent agreement with observations. The half-metallic character of the system for $|\omega|\leqslant 0.2$ is clearly seen from our computed results (inset to Fig. 2), in full accord[11] with recent experimental work.

The ferromagnetic character of the metallic state is clearly shown by using the DMFT propagators to compute the static part of the spin susceptibility $\chi_s(\mathbf{q})=N^{-1}\Sigma_{\mathbf{k}}G_{\uparrow}(\mathbf{k}+\mathbf{q})G_{\downarrow}(\mathbf{k})$, and the effective intersite exchange $J_{\text{eff}}(\mathbf{q})=J^2\chi_s(\mathbf{q})$. Given the small concentration of the correlated Mn ions, we expect that vertex corrections appearing normally in the computation of $\chi_s(\mathbf{q})$ will not modify our estimate of T_c much (these corrections scale with the Mn concentration). The transition temperature T_c is estimated from the DMFT equations.[5] We find, in full agreement with Ref. 16, that $T_c=0$ for $x=0,0.022$ and $T_c=120$ K for $x=0.043$.

In light of our results, we see clearly that ferromagnetism in $Ga_{1-x}Mn_xAs$ results from the interplay between two scales: the effective impurity bandwidth of the correlated solution (W_{eff}) and the local Hund interaction (J_H) with $J_H>W_{\text{eff}}$, putting the system in the DE class. As described above, this is out of scope of pure LDA- or LDA+U based approaches, which cannot access dynamical effects of strong electronic correlations and static (dynamic) disorder. A proper treatment of these dynamical processes plays a crucial role (via DMFT) in generating an impurity band with reduced bandwidth ($W<J_H$), stabilizing DE ferromagnetism in this DMS system.

Finally, we compute the optical conductivity $\sigma(\omega)$ di-

rectly from the fully renormalized DOS using the result known rigorously[17] in DMFT. In Fig. 3, we show our result $\sigma(\omega,T)$ as a function of ω for $x=0.043$. Concentrating on the T dependence, we see clearly that our results are very similar to the one from Ref. 13. In particular, the broad peak around 800 cm^{-1}, the smaller (antisite related) bump around 100 cm^{-1} (somewhat different from experiment), and the incoherent low-energy response are all in complete accordance with observations. More satisfyingly, the T dependence of the spectral weight transfer is also correctly reproduced: at low T (below T_c), no crossing point in $\sigma(\omega)$ is seen until 3000 cm^{-1}, while above T_c, the curves seem to cross around 800 cm^{-1}, in full semiquantitative agreement with experiment. However, we were not able to resolve a clear crossing point in the spectra above T_c. Finally, the distribution and T dependence of the optical spectral weight (decrease with increasing T below T_c, and increasing with T above T_c) is in good agreement with the data as well.

Given the detailed quantitative agreement of our results with those gleaned from various spectroscopic, optical, and magnetic measurements, we believe that we have provided a consistent, *ab initio* (LDA+correlations) description of $Ga_{1-x}Mn_xAs$. Our study highlights the importance of including intrinsic *and* extrinsic disorder, strong dynamical correlations and magnetic scattering, in concert with the real LDA band structure in one single picture. We have clearly shown how a consistent treatment of dynamical electronic correlations and disorder generates a narrow, quasicoherent impurity band in the semiconductor band gap, opening up the possibility for DE to drive the system into a ferromagnetic half-metallic state. Other diluted magnetic semiconductors of great current interest can be studied readily within this framework.

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