Magnetic circular dichroism from the impurity band in III-V diluted magnetic semiconductors

Jian-Ming Tang
Department of Physics, University of New Hampshire, Durham, NH 03824-3520

Michael E. Flatté
Department of Physics and Astronomy, University of Iowa, Iowa City, IA 52242-1479

The magnetic circular dichroism of III-V diluted magnetic semiconductors, calculated within a theoretical framework suitable for highly disordered materials, is shown to be dominated by optical transitions between the bulk bands and an impurity band formed from magnetic dopant states. The theoretical framework incorporates real-space Green’s functions to properly incorporate spatial correlations in the disordered conduction band and valence band electronic structure, and includes extended and localized electronic states on an equal basis. Our findings reconcile unusual trends in the experimental magnetic circular dichroism in III-V DMSs with the antiferromagnetic $p$-$d$ exchange interaction between a magnetic dopant spin and its host.

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In III-V diluted magnetic semiconductors (DMSs) such as Ga$_{1-x}$Mn$_x$As, formed by doping nonmagnetic host semiconductors such as GaAs with magnetic acceptors such as Mn, the magnetic properties are highly correlated with the electrical and optical properties \[1, 2, 3, 4\]. The effect of the added spin-polarized holes from the magnetic dopants on the relative optical absorption of right ($\sigma^+$) and left ($\sigma^-$) circularly polarized light (magnetic circular dichroism, or MCD) has been extensively explored to probe the interactions between the $d$ states of the local magnetic moments and the $p$ states of the host valence band \[5, 6, 7, 8, 9, 10, 11\]. Yet fundamental puzzles remain: the light polarization most absorbed in Ga$_{1-x}$Mn$_x$As, which determines the sign of the MCD signal, is different from that of Zn$_{1-x}$Mn$_x$Se. This suggests that the $p$-$d$ exchange interaction in Ga$_{1-x}$Mn$_x$As is ferromagnetic \[12\], however in the dilute limit the interaction between a Mn spin and the GaAs valence band is known to be antiferromagnetic \[12\]. Refs. \[7, 13\] argue the unexpected sign of the MCD signal can be reconciled with an antiferromagnetic $p$-$d$ interaction by considering a large shift of the Fermi level in the valence band due to doping (Moss-Burstein shift). However, the required Moss-Burstein shift is large (\sim 100 meV) and the MCD spectrum should have a pronounced doping dependence that includes changing sign at low doping \[9\], whereas the observed doping dependence of the dominant features of the MCD spectrum is weak \[9\] and the unexpected sign of the MCD signal is present in low-doped, paramagnetic Ga$_{1-x}$Mn$_x$As (even for $x \sim 0.005$) \[10\]. Furthermore, none of the above treatments adequately treat the role of disorder in the optical transitions, whereas measurements indicate the carrier mean free path to be less than 1 nm \[12\], comparable to the Fermi wavelength. Experimental evidence that the Fermi level in Ga$_{1-x}$Mn$_x$As lies in the impurity band rather than in the valence band \[15, 16, 17, 18, 19, 20, 21\] also requires reconsideration of the Moss-Burstein shift.

Here we find that a proper consideration of the strong spatially-localized perturbation of the electronic structure in the valence band due to the Mn dopant, including both the bound state of the acceptor and the perturbations of the continuum states near the dopant, is essential to accurately calculate the magnetic circular dichroism. A key element of the successful calculation of these properties is our approach to impurity averaging the optical absorption in magnetic semiconductors. Traditional approaches impurity average separately over the conduction band electronic structure and the valence band electronic structure, and then calculate the optical absorption for transitions between the two new effective bands as one would calculate optical absorption in a clean semiconductor. Instead we calculate the difference in optical absorption between the clean host and the host by calculating optical matrix elements between real-space Green’s functions for a single dopant before impurity averaging. The effect of the short mean free path is included naturally by restricting the real-space sum to a small cluster of approximately that diameter. Thus optical transitions that do not conserve crystal momentum are included without artificially relaxing momentum conservation between impurity-averaged bands \[8\].

In addition to obtaining the correct sign of the MCD signal for low doping as well as high doping, our calculations identify the dominant transitions contributing to the MCD to be transitions between the bulk bands and the acceptor states bound to the Mn (that will form the impurity band). These transitions would be forbidden if impurity averaging and momentum conservation in optical absorption calculations were improperly imposed, as both initial and final states would have different crystal momentum. We further find that the amplitude of the MCD tracks the magnetization of the material, as seen experimentally in the temperature-dependence of
eV (solid line), 0 eV (dotted line), and −0.1 eV (dashed line) relative to the valence-band maximum. The step increase near $M$ is the initial state energy $E_0$ and $M$ is the system volume, $\hat{p}$ is the momentum operator for an atomic site, and $l$ labels the atomic orbitals at each site. To simplify our calculations, we assume the momentum matrix elements are nonzero only between two Löwdin orbitals located at the same site and are independent of the type of the atom at that site. In the 16-band $sp^3$ tight-binding model we are left with only one type of momentum matrix element,

$$\langle \phi_{a_+l} | \hat{p}_z | \phi_{a_{-l}} \rangle = i P.$$  (4)

With the above simplifications $P$ can be linked directly to the momentum matrix element between the conduction and valence band Brillouin-zone-center states, known from bulk $k\cdot p$ theory. Therefore, no additional parameters are needed in our tight-binding framework needs to be introduced. The situation becomes more complex (and less empirically constrained) if momentum matrix elements between neighboring atomic sites are permitted to be non-zero. Using the tight-binding parameters in Ref. 27, the momentum matrix element between the zone-center states is $\langle \Gamma_{3vc} | \hat{p}_z | \Gamma_{1c} \rangle = 0.914 i P$. Thus we find $P^2/m = 17.3$ eV by setting the zone-center momentum matrix element to be the same as used in Ref. 28. We calculate the tight-binding Green’s functions with an energy linewidth of 10 meV as in Ref. 22. Lastly, we use a constant index of refraction, $n = 3.878$ for bulk GaAs at 2 eV [24] for the energy range (1.2-2.5 eV) shown in this Letter.

We first apply this method to calculate the absorption coefficient for bulk GaAs. In this case Eq. (2) can be evaluated exactly in momentum space and the results, $\alpha^\pm = \alpha_0$ and $M^\pm = M_0$, are shown in Fig. 1. A good agreement with the experimental data [30] as a function of the absorbed photon energy is found, although the calculated overall magnitude is larger by $\sim 50\%$, probably due to the slightly too large conduction band mass typically for tight-binding models of III-V semiconductors. The energy dependence near the absorption edge has a square-root dependence with an Lorentzian tail because the quasiparticles have a finite lifetime and excitons are not included in our calculations. At higher energy the absorption’s energy dependence is approximately linear. The shoulder near 1.9 eV is the onset for the split-off band (0.36 eV below the valence-band maximum). The absorption curves (solid and dotted lines) are approximately the same as long as the Fermi level is in the gap. If the Fermi level lies in the valence band, the absorption edge moves to higher energy and the shape is significantly altered. This shape change is not observed for

$$\hat{A}(E) = i 2\pi \left[ \hat{G}^R(E) - \hat{G}^A(E) \right].$$  (3)

The trace in Eq. (2) is taken over a set of Löwdin orbitals, $\phi_{a_{\pm l}}(\mathbf{r} - \mathbf{R}_{j,a})$, where $j$ labels the primitive unit cells, $a$ labels the atomic sites within a unit cell, $\mathbf{R}_{j,a}$ is the position vector of an atomic site, and $l$ labels the atomic orbitals at each site. In the 16-band $sp^3$ tight-binding model we are left with only one type of momentum matrix element,

$$\langle \phi_{a_{+l}} | \hat{p}_z | \phi_{a_{-l}} \rangle = i P.$$  (4)
Mn interactions are broader in energy than the energy splittings due to Mn-Mn interactions. This approximation is sufficient for describing structures in the optical absorption that are associated with the transition of an electron to or from the impurity level. From Fig. 3 it is apparent that both the small broadening factor (10 meV) that we used for the processes between the valence and conduction band, and the energy linewidth in the single-particle Green’s function. Therefore, the overall calculated MCD magnitude we obtain is larger than experimentally measured.

The processes between the valence and conduction band occur at the four 1st-nearest-neighbor sites. The acceptor states are almost fully spin polarized and split into three energy levels due to the spin-orbit interaction[22]. As a result, the three levels have quite distinct orbital-angular-momentum character, and the top and bottom levels are coupled to opposite polarizations of circularly-polarized light. The upper level (farthest from the valence band edge) has orbital angular momentum parallel to spin.

Our MCD results were obtained with a quasi-spherical cluster enclosing 99 atoms, with one Mn atom in the center. Up to the 8th nearest neighbors are included, which are 8 Å away from the Mn. ~ 70% of the acceptor state is included in this cluster, which corresponds to approximately 2% Mn concentration. The results for different hole carrier concentrations are shown in Fig. 2 and we can see that the relative size of $\alpha^{-}$ is always larger than $\alpha^{+}$, no matter the doping. Note that we have ignored the orbital mixing in the impurity band by Mn-Mn interaction, which would reduce the MCD, and the energy broadening is taken into account only through a 10 meV linewidth in the single-particle Green’s function. Therefore, the overall calculated MCD magnitude we obtain is larger than experimentally measured.

To understand the nature of the doping-independent “positive” ($\alpha^{-} > \alpha^{+}$) MCD signal, the contributions from different optical transitions at the typical photon energy (2 eV) are shown in Fig. 3 as a function of the initial-state energy. Two peaks for each circularly-polarized light are present, corresponding to the processes associated with the transition of an electron to or from the impurity levels. In our configuration, the upper impurity level has predominately angular momentum projection $-1$ and the bottom level has projection $+1$ because the spin-orbit interaction favors the orbital angular momentum parallel to spin (in the valence electron convention). The processes between the valence and conduction band are indicated by the short arrow in Fig. 3. The sharpness of the peaks of $M$ in the energy space comes from the small broadening factor (10 meV) that we used for the impurity level. From Fig. 3 it is apparent that both $\sigma^{+}$ processes are suppressed by the Pauli exclusion prin-
FIG. 3: (color online) The optical transition strength, \( \Delta M^+(E, E + h\omega) \) (dashed line), and \( \Delta M^-(E, E + h\omega) \) (solid line), as functions of \( E \) with \( h\omega = 2 \) eV. The four peaks correspond to the four distinct processes shown by the arrows in the energy diagram at the center. States in the shaded region are occupied if the Fermi level lies in the impurity band.

FIG. 4: (color online) The absorption-coefficient differences, \( \Delta \alpha^+ \) (dashed line), \( \Delta \alpha^- \) (dash-dotted line), and \( \alpha^- - \alpha^+ \) (solid line), with \( h\omega = 2 \) eV as a function of the Fermi level relative to the valence-band maximum.

There is no sharp absorption onset due to transitions from the valence band to the impurity band and the dominant MCD features are proportional to the material magnetization, as previously reported from experimental observations.

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