Magneto-optics in pure and defective $Ga_{1-x}Mn_xAs$ from first principles

S. Picozzi,[1] A. Continenza,[1] M. Kim,[2,3] and A. J. Freeman[2]
[1]*INFM-CNR, CASTI Regional Lab. and Dip. Fisica, Università degli Studi dell'Aquila, 67100 Coppito (L'Aquila), Italy*
[2]*Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60208, USA*
[3]*Department of Physics, Seoul National University, Seoul, Korea*
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The magneto-optical properties of $Ga_{1-x}Mn_xAs$ including their most common defects were investigated with precise first-principles density-functional full-potential linearized augmented plane wave calculations in order to: (i) elucidate the origin of the features in the Kerr spectra in terms of the underlying electronic structure; (ii) perform an accurate comparison with experiments; and (iii) understand the role of the Mn concentration and occupied sites in shaping the spectra. In the substitutional case, our results show that most of the features have an interband origin and are only slightly affected by Drude-type contributions, even at low photon energies. While not strongly affected by the Mn concentration for the intermediately diluted range ($x \sim 10\%$), the Kerr factor shows a marked minimum (up to 1.5°) occurring at a photon energy of ~0.5 eV. For interstitial Mn, the calculated results bear a striking resemblance to the experimental spectra, pointing to the comparison between simulated and experimental Kerr angles as a valid tool to distinguish different defects in the diluted magnetic semiconductors framework.

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The magneto-optical (MO) Kerr effect has been known since 1877 when Kerr[1] observed that linearly polarized light reflected from a magnetic surface becomes elliptically polarized with the major axis rotated with respect to the incident light. The Kerr effect, as well as other closely related spectroscopic effects, such as the Faraday effect and magnetic circular dichroism, can be traced back to the different interaction of left- and right-circularly polarized light with a magnetized solid. MO effects are therefore powerful experimental probes that play a relevant role in clarifying the electronic structure of ferromagnets and providing detailed information on the influence of broken time-reversal symmetry in itinerant quasiparticle electron states.[2,3]

Within the fascinating field of semiconductor spintronics,[4] transition metal doped semiconductors, due to their unusual magnetic and electronic properties, have been the focus of intense research in the last few years. The early prototype material is undoubtedly $Ga_{1-x}Mn_xAs$,[5] a dilute magnetic semiconductor (DMS) with $x < 10\%$, and a Curie temperature <150 K, for which its ferromagnetism is generally explained in terms of a hole-carrier-mediated exchange mechanism. Although the electronic and magnetic properties of $Ga_{1-x}Mn_xAs$ have been extensively studied, to our knowledge *ab initio* calculations for the MO properties of $Ga_{1-x}Mn_xAs$ have not been reported. The focus of this work is therefore to perform an accurate comparison with extensively performed experiments,[6–8] in order to: (i) assess the validity of the first-principles electronic structure theory and (ii) explain the main features in the MO spectra of GaMnAs on the basis of its electronic structure.

In our approach based on the local spin density approximation to the density functional theory (DFT), the Kohn-Sham equations are solved self-consistently using the highly accurate full-potential linearized augmented plane wave (FLAPW)[9] method. Spin-orbit coupling (SOC), essential to describe MO effects, neglected in the self-consistent cycle, is included as a second variational step[10] in the evaluation of the optical conductivity tensor, σ_{ij},[11] starting from DFT eigenvalues and eigenvectors [see Eq. (1)]. For metals (or half-metals, such as GaMnAs), the components of the optical conductivity tensor are given by a sum of interband and intraband contributions. The interband transitions are obtained according to the Kubo formalism within linear response theory through momentum matrix elements Π_{ij}:[2]

$$\sigma_{\alpha\beta}(\omega) = \frac{i}{\omega V}\int \frac{d\mathbf{k}}{(2\pi)^3}\sum_{i,j}\left(\frac{\Pi_{ji}^{\alpha}\Pi_{ij}^{\beta}}{\omega + i/\tau - \epsilon_{ij}} - \frac{\Pi_{ij}^{\alpha}\Pi_{ji}^{\beta}}{\omega + i/\tau + \epsilon_{ij}}\right), \quad \alpha,\beta = x,y,z, \tag{1}$$

where ω is the photon energy, $\epsilon_{ij}=E_i-E_j$ is the difference between eigenvalues for states i and j, V is the volume of the unit cell, and τ is the interband relaxation time. The momentum operator is defined as

$$\Pi_{ij}^{\alpha} = \int \phi_{i,\mathbf{k}}^{*}(\mathbf{r})\left[\nabla^{\alpha} + \left(\frac{1}{4m}\right)(\sigma \times \nabla V(\mathbf{r}))\right]\phi_{j,\mathbf{k}}(\mathbf{r})d\mathbf{r}, \tag{2}$$

where $\phi_{i,\mathbf{k}}$ is the eigenvector for state i and point $\mathbf{k}$ of the Brillouin zone. For simplicity, the $\mathbf{k}$ dependence of both Π_{ij} and ϵ_{ij} is understood and not explicitly reported in Eqs. (1) and (2). The effect of the second term in Eq. (2), arising from the fully relativistic treatment of the interaction Hamiltonian, is generally assumed to be small and will therefore be neglected here.

The intraband contribution is added to the diagonal components of the conductivity tensor with a phenomenological Drude expression: $\sigma_D = \omega_p^2/4\pi(1 - i\omega\tau_D)$ where the plasma frequency is given by: $\omega_{p,\alpha}^2 = (4\pi e^2/V)\Sigma_{i\mathbf{k}}\delta(\epsilon_{i\mathbf{k}} - E_F)|\Pi_{ii}^{\alpha}|^2$ (E_F is the Fermi energy and τ_D is the intraband relaxation time). Since all the considered unit cells show a cubic symmetry (see below), all the directions $\alpha = x, y, z$ show the same plasma frequency (i.e., $\omega_{p,\alpha} = \omega_p$). In order to accurately calculate ω_p, we used the procedure proposed in Ref. 12: the eigenenergies E_i (the $\mathbf{k}$ dependence is understood) calculated

on 216 **k** points were used for a spline fitting of the bands over the Brillouin zone. The resulting interpolating Fourier series was then used to calculate the derivative required in the evaluation of ω_p. We furthermore note that, since the systems of interest show half-metallicity (i.e., the density of states in the minority spin channel shows a gap in proximity to E_F), only majority spin-states that cross the Fermi level contribute to the plasma frequency.

Here, we only consider the Kerr effect in the so-called *polar geometry*, in which the incident wave vector and magnetization are perpendicular to the surface. In this case, the Kerr rotation angle $\theta_k(\omega)$ and its ellipticity $\eta_k(\omega)$ can be obtained from the conductivity tensor as follows:[3]

$$\theta_k(\omega) + i\,\eta_k(\omega) = -\frac{\sigma_{xy}(\omega)}{\sigma_{xx}(\omega)\sqrt{1 + i(4\pi/\omega)\sigma_{xx}(\omega)}}. \qquad (3)$$

In order to investigate the effect of Mn concentration on the MO properties, we considered different unit cells (each containing a single Mn impurity and with the GaAs experimental lattice constant, $a=10.69$ a.u.): in the 6.25% Mn-concentration case (i.e., 32 atoms per cell), the bcc unit cell had the Bravais lattice $\mathbf{a}_1=(a,a,-a)$, $\mathbf{a}_1=(-a,a,a)$, $\mathbf{a}_3=(a,-a,a)$, whereas in the 12.5% case (i.e., 16 atoms per cell) the fcc cell had Bravais lattice $\mathbf{a}_1=(a,a,0)$, $\mathbf{a}_2=(a,0,a)$, $\mathbf{a}_3=(0,a,a)$.

We used a basis set of plane waves with wave vector up to $K_{\max}=3.5$ a.u. and an angular momentum expansion up to $l_{\max}=8$ for both the potential and charge density. The muffin-tin radius, R_{MT}, for Mn, Ga, and As was chosen equal to 2.1, 2.3, and 2.3 a.u., respectively. The Brillouin zone (Bz) was sampled using a (4,4,4) Monkhorst-Pack[13] cubic shell, whereas the optical conductivity was computed using 216 special **k** points. As for the Drude term in the optical conductivity, we used our calculated plasma frequency $\omega_p \sim 1.5$ eV and an intraband relaxation time $\hbar/\tau_D=0.3$ eV. In order to investigate the effects of the most common defects on the MO properties, we also considered 32-atom cells with (i) an interstitial Mn, (ii) an As-antisite, i.e., a substitutional Mn located at the origin along with an As-antisite located at $(a/2,a/2,0)$, and (iii) an interstitial-substitutional dimer coupled antiferromagnetically. Although, according to DFT predictions, the most energetically favorable site is the substitutional one, the possibility for some Mn to occupy the interstitial sites and that As antisites are formed during severely-out-of-equilibrium growth cannot be ruled out, as several experiments appear to show.[14]

We first focus on the most diluted systems ($x=6.25\%$) with Mn in the substitutional position; these can presumably be well compared with available experiments.[7,8] Figure 1(a) shows the real part of the complex Kerr angle as a function of frequency.

Let us recall that the interband parameter τ mainly contains "lifetime" effects, whose estimation from first principles is very complex (requiring an accurate treatment of many-body effects and excited states) and definitely beyond the scope of the present work. Moreover, as shown in Eq. (1), the τ parameter appears in the denominator of the conductivity formula in the expression of the energy conservation required for optical transitions, therefore taking into account the effect of phonons and magnons through which the energy exchange induced by the incoming photon might occur; the experimental resolution, along with temperature effects, are also included in this parameter. Therefore, in order to highlight the effect of τ on the spectra, we show the results for two different values of τ (both physically meaningful), in the limit of (i) smaller [dashed line in Fig. 1(a)] and (ii) larger [solid line in Fig. 1(a)] effects of excited state lifetime, experimental broadening, etc. The remarkable thing is that, for a small broadening of $\hbar/\tau=0.1$ eV, the Kerr rotation can reach values of more than 1.5°: this unexpectedly high Kerr rotation may open the way to magneto-optical applications using DMS. However, it is also evident that the maximum value of the Kerr rotation is markedly dependent on the smearing value used: already with a larger broadening ($\hbar/\tau=0.3$ eV), the Kerr rotation shows a value of the order of 0.5°, typically observed in $3d$ ferromagnets.[3] Finally, we also note that our calculated spectrum using the smaller broadening is in remarkable agreement with model calculations[15] based on a Kohn-Luttinger Hamiltonian and a kinetic ex-

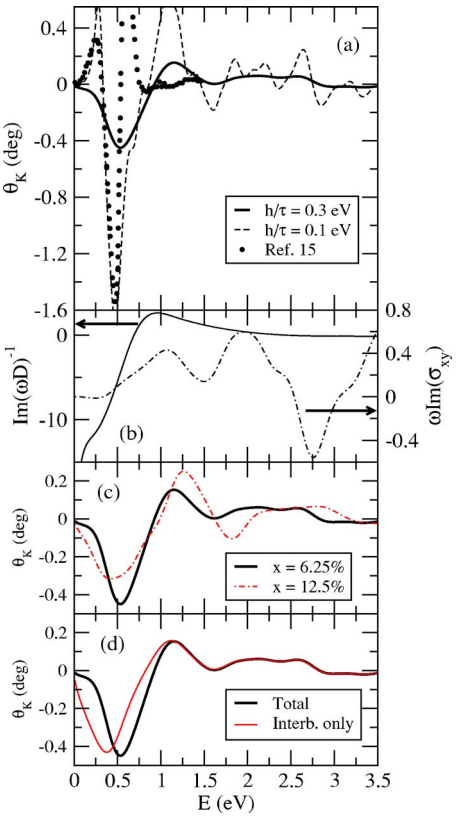

FIG. 1. (Color online) (a) Calculated Kerr rotation for Mn in the substitutional site for different smearings—of 0.1 eV (dashed line) and 0.3 eV (bold solid line)—as a function of energy. Circles denote values from model calculations (Ref. 15). (b) Kerr rotation broken down in imaginary parts of numerator (i.e., MO part, dot-dashed line, right y axis) and inverse denominator (i.e., optical part, solid line, left y axis), see the text for details. (c) Effect of Mn concentration: $x=6.25\%$ (bold solid line) and $x=12.5\%$ (dot-dashed line). (d) Comparison between total (interband+intraband) contributions (bold solid line) and interband only (thin solid line).

change interaction—not only the spectral shape, but also the energy position of the peaks is in good coincidence.

The peculiar shape of the Kerr rotation, with the strong resonance at ~0.5 eV and several other features at higher energies, can be fully explained in terms of the imaginary parts of the numerator $(\omega\sigma_{xy})$ and denominator $[\omega D = \omega\sigma_{xx}(\omega)\sqrt{1+i(4\pi/\omega)\sigma_{xx}(\omega)}]$ in Eq. (3), therefore separating the MO and optical contributions, respectively [see Fig. 1(b)]. The deep resonance at ~0.5 eV can be ascribed to the minimum of the denominator, whereas the other peaks follow the numerator trend, in turn due to the interplay of the SOC and exchange splitting. The strong resonance at low energies has therefore an "optical" origin, whereas the high energy part is instead due to MO effects.

In order to further investigate the MO properties and, in particular, the effect of the Mn concentration, we show in Fig. 1(c) the calculated Kerr rotation and ellipticity, for the 6.25% and 12.5% case. The overall trend as a function of frequency is quite similar for the two concentrations,[16] confirming that in this intermediate diluted regime the concentration of magnetic impurities does not strongly affect the electronic structure—consistent with previous reports.[17] In particular, the principal features for relevant energies <2 eV are present in both concentration cases—the peaks only differ in their energy position. This rather weak dependence on concentration was already noted from the experiment by Lang *et al.*[8] that measured a Kerr rotation that is comparable in size upon more-than-doubling the concentration (i.e., Kerr spectra were measured for $x=0.014$ and 0.03), although some of the features as a function of energy varied significantly with the concentration.

Finally, in order to investigate whether the presence of the strong resonance—given its relatively low energy—is due to an intraband or interband contribution, the Kerr rotation without the Drude contribution is also shown (see bold versus thin line) in Fig. 1(d). As expected, the exact position of the peak is affected by the Drude contribution (or, equivalently, by the plasma frequency) but the deep resonance is kept and is therefore seen to have mainly an interband origin.

Moreover, it is of interest to compare our results for the substitutional case (see the first column in Fig. 2) with available experimental spectra, measured in the very diluted limit $(x\sim 1\%-3\%)$[8] as well as for a concentration similar to this work $(x\sim 6\%)$.[7] Although the order of magnitude is consistent, there are some discrepancies between theory and experiment. In particular, the experimental Kerr rotation is always negative, whereas theoretical spectra show some crossing with the zero y axis. However, the energy position of the minimum at ~1.5–2 eV and of the maximum at ~2.5–3 eV is reproduced in our spectra.

As for the Kerr ellipticity, there are some similarities between theory and experiment regarding the crossing of the zero axis as well as the order of magnitude, but also some severe discrepancies (especially in the low energy range). There might be several reasons for this disagreement, among which we mention: (i) the poor description of features in the DFT electronic structure related to excited or correlated states[18] and (ii) the fact that the calculations should be compared with experiments at zero temperature. Indeed, most of the measurements were performed at higher temperatures, where the magnetization is expected to be smaller, thus resulting in a smaller Kerr angle. As a confirmation of that, we recall that experiments by Kojima *et al.*[7] were performed at 77 K on samples showing a Curie temperature of 110 K (and, therefore, the measurements were done at a temperature not much lower than T_C); on the other hand, experiments by Furdyna *et al.* were performed at 1.8 K on samples with a ferromagnetic Curie temperature of 60 K: in this case, the samples clearly show a saturated magnetization. As a result, the Kerr signal in the latter case is higher than in the former case; moreover, consistent with this temperature dependence, our results—which ideally reproduce the situation at 0 K or, at least, in the condition of saturated magnetization—predict a rather high value of the Kerr angle.

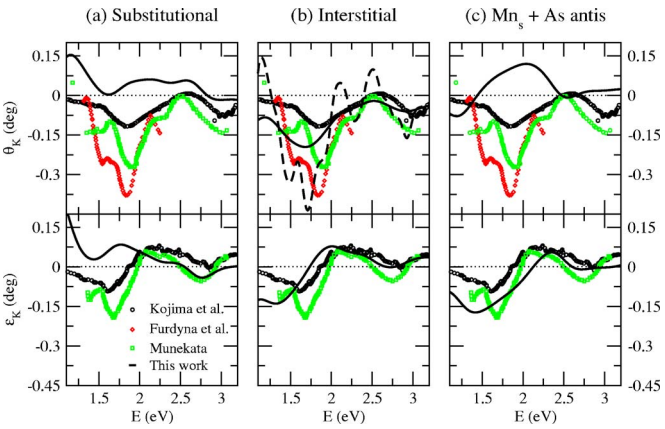

FIG. 2. (Color online) Calculated complex Kerr angle (thin solid line) for an energy broadening of 0.3 eV: rotation (upper panels) and ellipticity (lower panels) for (a) substitutional Mn, (b) interstitial Mn, and (c) substitutional Mn along with an As antisite. Experimental data are marked by symbols: circles, diamonds, and stars for Refs. 7, 8, and 6, respectively. In panel (b), we also show the Kerr rotation calculated with a small broadening ($\hbar/\tau=0.1$ eV, see the dashed line).

The disorder that might be present in the samples is another reason that could explain the discrepancy between theory and experiment. Therefore, in order to investigate the effects of the most common defects on the MO properties, we also show in Fig. 2 the calculated Kerr angles for (b) the interstitial Mn and (c) substitutional Mn along with an As-antisite. Clearly, different Mn positions or the presence of antisites significantly change the spectra, pointing to a possible use of the MO Kerr effect to distinguish substitutional and interstitial Mn, antisites, etc. In particular, it is immediately evident that there is a very good agreement as far as the Kerr rotation and ellipticity are concerned for the interstitial case—as is evident both with small and large broadenings (see dashed and solid line in Fig. 2) used to better reproduce the experiments by Furdyna and Kojima, respectively. This might be explained as follows: most of the samples[7] were annealed and it is well known that annealing brings interstitials to the surface. Therefore, the Kerr technique, which mostly probes the surface samples, sees an enhanced contribution from the interstitials. As far as the ellipticity only is

concerned, we note that a generally satisfactory agreement is reached also in the As-antisite case. We do not provide plots for the interstitial-substitutional Mn dimers, since the agreement is rather poor, as expected. In fact, this is compatible with the idea that the samples in Ref. 7 were annealed at 280 °C, and so the dimers—possibly formed during the low-temperature growth—are expected to separate and to no longer exist in such an appreciable density as to give a strong contribution to the Kerr spectra.

Finally, we point out that our DFT-FLAPW simulations for hexagonal MnAs, which are in good agreement with previously published spectra[19] and therefore not reported here, show a much larger (on the order of 0.5° over the whole energy range) Kerr rotation and ellipticity—and strikingly different from experiments for $Ga_{1-x}Mn_xAs$. Therefore, the comparison between theory and experiment confirms that the Kerr signal is not due to precipitates in the samples and suggests that this kind of simulation is a valid tool to reveal competing phases that can frequently occur during DMS growth.[20]

In summary, accurate FLAPW calculations within density functional theory and the Kubo formalism were performed focusing on the optical and magneto-optical properties of GaMnAs. The maximum Kerr angle, occurring at a photon energy of <0.5 eV, can reach high values ($>1.5°$) and is mainly due to an optical rather than a magneto-optical origin. In the intermediate diluted regime ($x \sim 10\%$), the Kerr spectra do not depend dramatically on concentration and are mostly due to interband, rather than intraband, contributions. For Mn in the substitutional position, the comparison with experiments for the Kerr rotation and ellipticity shows some disagreement. On the other hand, the spectra are quite well reproduced for interstitial Mn, suggesting that the Kerr effect might be used to distinguish the MO response of substitutional rather than interstitial Mn. However, the role that the somewhat inaccurate treatment of correlation or many-body effects within a single-particle DFT description of the GaMnAs electronic structure might have in shaping the Kerr spectra has still to be investigated.

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