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Dilute ferrimagnetic semiconductors in Fe-substituted spinel ZnGa_2O_4

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Abstract

Solid solutions of nominal composition $[\text{ZnGa}_2\text{O}_4]_{1-x}[\text{Fe}_3\text{O}_4]_x$, of the semiconducting spinel ZnGa_2O_4 with the ferrimagnetic spinel Fe_3O_4 , have been prepared with $x = 0.05, 0.10$, and 0.15 . All samples show evidence for long range magnetic ordering with ferromagnetic hysteresis at low temperatures. The magnetization as a function of field for the $x = 0.15$ sample is S-shaped at temperatures as high as 200 K. Mössbauer spectroscopy of the $x = 0.15$ sample confirms the presence of Fe^{3+} , and spontaneous magnetization at 4.2 K. The magnetic behaviour is obtained without greatly affecting the semiconducting properties of the host; diffuse reflectance optical spectroscopy indicates that Fe substitution up to $x = 0.15$ does not affect the position of the band edge absorption. These promising results motivate us to suggest the possibility of dilute ferrimagnetic semiconductors which do not require carrier mediation of the magnetic moment.

1. Introduction

The burgeoning field of spintronics [1, 2] has created demands for entirely new classes of materials. One such materials class combines both semiconducting and ferromagnetic properties. Magnetic semiconductors can help in the efficient injection of spin from a ferromagnetic contact to a semiconductor [3]. The substitution of magnetic ions such as Mn^{3+} in traditional semiconducting materials such as GaAs is a well-established route to making ferromagnetic semiconductors [4, 5]. However, Mn-substituted GaAs as well as digital heterostructures such as GaAs/0.5 ML Mn [6] have maximum Curie temperatures of around 100 K or less. In the ideal case, we desire magnetic semiconductors with a magnetic transition above room temperature. The ability to have both n- and p-type doping, a long spin-relaxation

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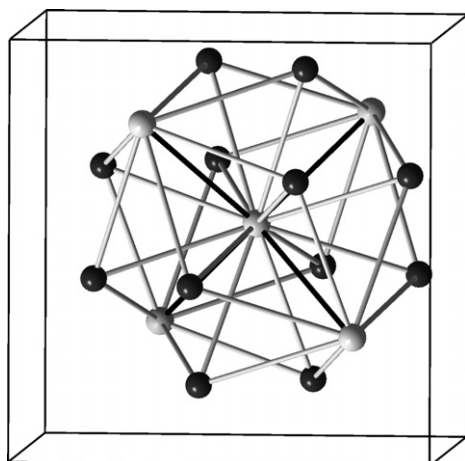


Figure 1. A cation cluster centred around an tetrahedral A atom (light grey spheres) in the spinel crystal structure. The dark grey spheres are the octahedral B atoms. Within a 3.7 Å distance, each octahedral Ga atom in ZnGa_2O_4 has 12 tetrahedral Zn neighbours and 4 Ga neighbours.

lifetime, and large carrier spin polarization are other desirable features. Proposed candidate materials are strongly hole-doped wide band gap wurtzite semiconductors GaN and ZnO, with magnetic transition metal tM substituents on the cation sites [7, 8]. A number of recent studies on bulk and thin-film samples have ensued which suggest that ZnO:tM with tM = Co [9–11] and with tM = Mn [12, 13] are ferromagnetic at room temperature, whilst others find spin-glass behaviour [14, 15].

Results of our prior work on bulk samples of ZnO:tM systems suggest a complete absence of any magnetic ordering in well-characterized bulk samples [16, 17]. Studies by Kolesnik *et al* confirm these findings [18]. Careful density functional calculations by Spaldin [19] also point to difficulties in inducing ferromagnetism by transition metal substitution in ZnO. We find that while magnetic susceptibility indicates strong near neighbour coupling in ZnO:tM (tM = Mn and Co), the mean field coupling is exceedingly weak [17]. It is the mean field term that would dictate magnetic ordering. It is useful to temper expectation with the following observation: the few known ferromagnetic oxide semiconductors have rather low T_C s: BiMnO₃ ($T_C = 105$ K) [20], SeCuO₃ ($T_C = 26$ K) [21], YTiO₃ ($T_C = 29$ K) [22], EuO ($T_C = 79$ K) [23].

A promising alternative is to induce *ferrimagnetism* in a wide band gap semiconductor with *two* host cation sites: this would exploit the more natural tendency of spins in insulating oxides to anti-align and would require no conduction electrons. A natural structure for ferrimagnetism is spinel, AB_2O_4 , where spins in the tetrahedral (A) and octahedral (B) cation sites are usually anti-aligned with respect to each other; in addition, with two B sites for every A site, the possibility of a net ferrimagnetic moment exists. Figure 1 shows the cation network centred around a single tetrahedral A cation in the spinel structure. The very high effective cation coordination in this structure type would mean that even at rather low concentrations of substituent transition metal ions, extensive magnetic coupling can be expected. In this contribution, we have chosen spinel ZnGa_2O_4 with a direct band gap of 4.1 eV as host [24]. Both ZnGa_2O_4 and ZnO can be grown epitaxially on spinel MgAl_2O_4 substrates [25, 26], suggesting that the title compound can be incorporated in devices.

By preparing nominal solid solutions $[\text{ZnGa}_2\text{O}_4]_{1-x}[\text{Fe}_3\text{O}_4]_x$ ($0 \leq x \leq 0.15$), we have been able to induce magnetism, with strongly hysteretic behaviour for the $x = 0.15$ sample

at 5 K. Mössbauer spectra acquired at 293 and 4.2 K for the $x = 0.15$ sample suggest spontaneous magnetization at 4.2 K. The data also reveal the complete absence of Fe²⁺ in the sample, which supports our view of dilute ferrimagnetism rather than magnetism arising from a spurious source such as magnetite Fe₃O₄ nanoparticles in a ZnGa₂O₄ matrix. Diffuse reflectance UV/visible spectroscopy reveals that the direct band gap of ZnGa₂O₄ is unaffected by substitution.

2. Experimental results

As in previous work on polycrystalline Zn_{1-x}M_xO materials [16, 17], precursor oxalates Zn_{1-x}Fe_x(C₂O₄)·2H₂O were prepared with $x = 0.00, 0.02, 0.05, 0.10,$ and 0.15 by precipitation from aqueous solution. Polycrystalline samples with the nominal compositions [ZnGa₂O₄]_{1-x}[Fe₃O₄]_x ($0 \leq x \leq 0.15$) were made by grinding together the corresponding oxalate with appropriate amounts of Ga₂O₃ and decomposing in air at 1473 K for 18 h, with an intermediate regrinding step. For $x = 0.00$, the powder is white; as x increases, the powder colours range from beige to auburn. Beyond $x = 0.15$, samples require longer sintering times, suggesting a possible solubility limit in the vicinity. Step-scanned x-ray diffraction data on the powders were collected on a Scintag X-2 diffractometer operated in the θ - 2θ geometry. Transmission electron microscopy of the $x = 0.15$ sample, in conjunction with energy dispersive x-ray spectroscopic (EDX) analysis, was carried out on a JEOL JEM 2010 microscope. The sample powder was dispersed from a solvent onto a carbon-coated copper grid for TEM studies. UV/visible diffuse reflectance spectra were acquired for powders sprinkled on Scotch tape. Magnetization data were collected on a Quantum Design MPMS 5XL SQUID magnetometer operated between 2 and 400 K. Mössbauer spectra were collected at 293 and 4.2 K using a constant-acceleration spectrometer equipped with a 1024-channel analyser and operated in the timescale mode. The γ source was 25 mCi ⁵⁷Co/Rh. The spectra were analysed using the computer program EFFINO [27].

3. Results and discussion

X-ray diffraction data, plotted on a log scale in figure 2(a), indicate a very small amount of as yet unidentified impurity at $34.2^\circ 2\theta$ in all the samples, including the non-magnetic host ZnGa₂O₄. In addition, the $x = 0.15$ sample has a small amount of the impurity monoclinic Ga₂O₃ (PDF Card 41-1103). Other than these clearly non-magnetic impurities, the samples are clean, showing only the spinel phase. The diffraction profiles could be satisfactorily fitted to the spinel crystal structure by the Rietveld method using the XND program [28]. For all the samples, the reliability factor (R_{Bragg}) was less than 7%. The evolution of the a cell parameter with x is shown in figure 2(b) and is consistent with substitution of Fe on the spinel ZnGa₂O₄ lattice. The line connects published cell parameters of ZnGa₂O₄ [29] and Fe₃O₄ [30]. Under the conditions of our preparation, Fe₃O₄ is stable under the heat treatment conditions which we have employed [31], so we were initially confident in describing the Fe substitution as a solid solution [ZnGa₂O₄]_{1-x}[Fe₃O₄]_x. However, as we shall describe presently, the Mössbauer spectra indicate a complete absence of Fe²⁺ in the $x = 0.15$ sample. We do see a small broadening of the x-ray profiles with substitution characteristic of the increased number of elements in the crystal. The x-ray form factors of Fe, Zn, and Ga are too similar to one another for us to directly refine the relative amounts of these elements in the spinel crystal structure.

TEM/EDX analysis of the $x = 0.15$ sample systematically indicated that the Fe:Zn:Ga atomic ratio was close to 1:3:6 rather than the ratio calculated from the nominal composition

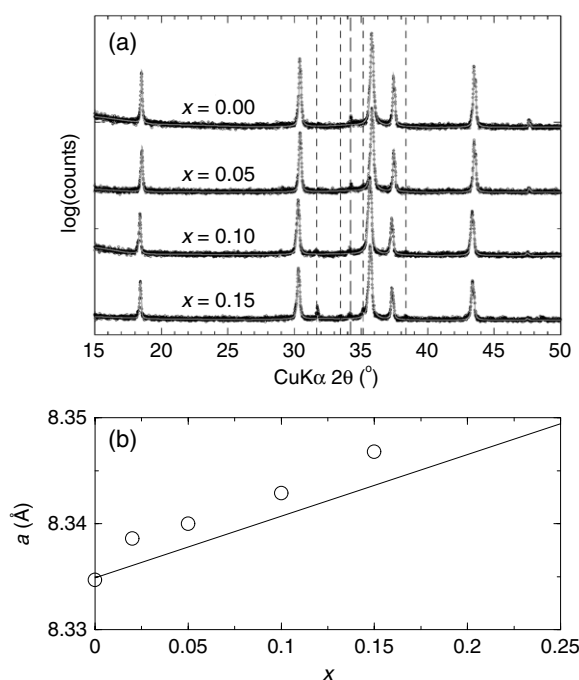


Figure 2. (a) Powder x-ray diffraction patterns of the nominal samples $[\text{ZnGa}_2\text{O}_4]_{1-x}[\text{Fe}_3\text{O}_4]_x$ ($x = 0, 0.05, 0.10,$ and 0.15) displayed on a log scale. Points are data and the line is the Rietveld fit to the spinel crystal structure. The four dashed vertical lines indicate a very small impurity content of monoclinic Ga_2O_3 . The long dashed line at $34.2^\circ 2\theta$, common to all the samples, arises from an unidentified non-magnetic impurity. (b) Circles display the evolution of the spinel lattice parameter with x in the region $0 \leq x \leq 0.15$. The line connects the published cell parameter of spinel ZnGa_2O_4 at $x = 0$ with the published cell parameter of spinel Fe_3O_4 at $x = 1$.

which is 1:1.9:3.8, or nearly 1:2:4. More importantly, the samples are homogeneous on the length scale of the EDX spot size (approximately 3 nm), consistently displaying the same ratios over several spots.

Across the substitution series, the semiconducting nature of ZnGa_2O_4 is retained as confirmed by UV/visible diffuse reflectance spectroscopy. Diffuse reflectance UV/visible spectra across the series are shown in figure 3. ZnGa_2O_4 is a direct band gap semiconductor [24], as confirmed by the sharp band edge absorption. In our samples we find the band edge is at 3.3 eV rather than the reported value of 4.1 eV. However, it is well known [24] that ZnGa_2O_4 displays a very sensitive dependence of the optical absorption edge on composition, and a very small concentration of cation vacancies are sufficient to shift the edge to the red. Substitution with iron leaves the band edge absorption unchanged, though new features associated with atomic transitions arise in the visible region. The relative rise of these new features in the visible region of the spectrum results in an effective *relative* decrease in the intensity of the band edge absorption.

Figure 4(a) shows the temperature dependence of the magnetization for three samples, $x = 0.05, 0.10,$ and 0.15 . The magnetization has been scaled by the mole number of Fe_3O_4 ; this implies that in the absence of long range interactions, traces for the three samples should collapse onto a single curve. We do not observe this even at 400 K. Plots of $1/M$ as a function of T are not linear for any of the samples below 400 K, also in accord with the existence of

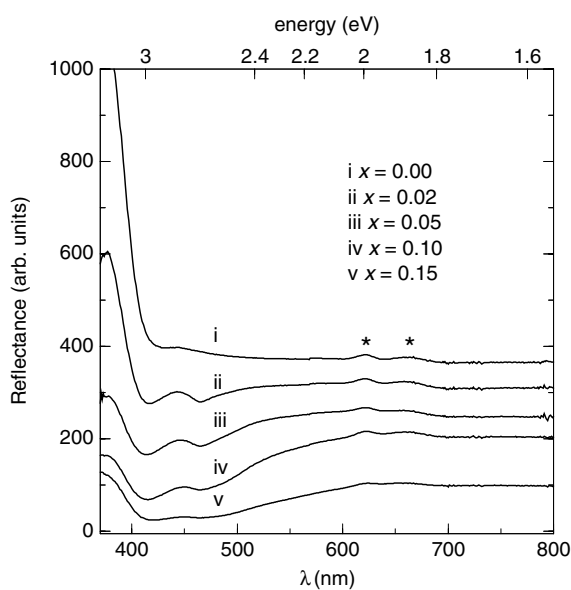


Figure 3. Diffuse reflectance UV/visible spectra of $[\text{ZnGa}_2\text{O}_4]_{1-x}[\text{Fe}_3\text{O}_4]_x$ for the different x in the near UV and visible regions of the spectrum. Data have been offset along the reflectance axis for clarity. The asterisks are associated with the absorption of the Scotch tape.

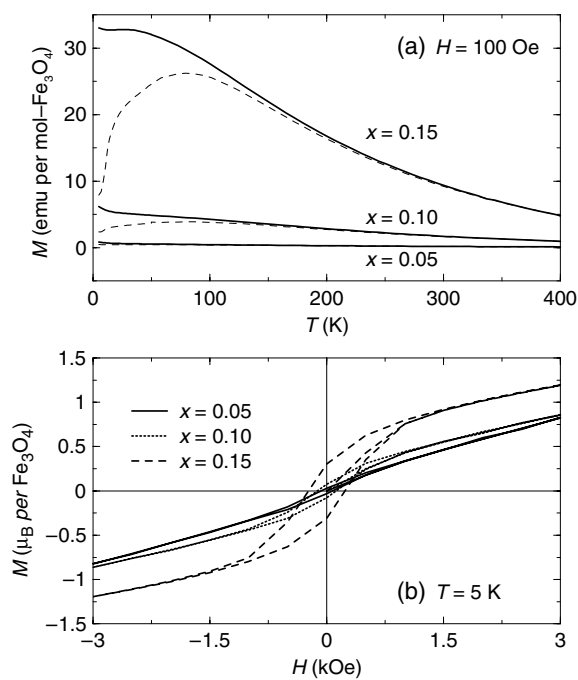


Figure 4. (a) Magnetization under a 100 Oe field as a function of temperature for $[\text{ZnGa}_2\text{O}_4]_{1-x}[\text{Fe}_3\text{O}_4]_x$ with $x = 0.05, 0.10,$ and 0.15 . Data were collected upon warming after cooling under zero field (broken curves) and after cooling under a 100 Oe field (solid curves). (b) The 5 K magnetization of the three samples.

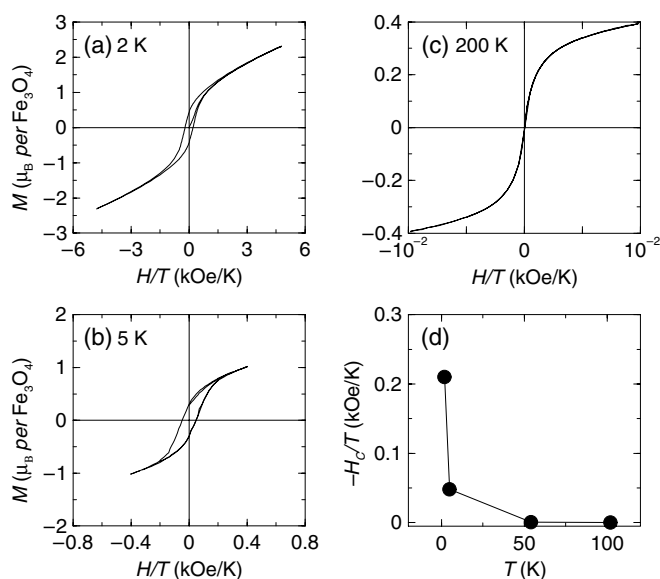


Figure 5. ((a)–(c)) Magnetization as a function of H/T of $[\text{ZnGa}_2\text{O}_4]_{1-x}[\text{Fe}_3\text{O}_4]_x$ with $x = 0.15$ at different temperatures (indicated). (d) Coercive field scaled by temperature at different temperatures for the $x = 0.15$ sample.

long range interactions. All three samples show a separation of the ZFC and FC traces. This is clearly visible for $x = 0.10$ and 0.15 at about 100 K. At 5 K, all three samples display hysteretic behaviour, as seen in figure 4(b). None of the samples show magnetic saturation, indicating that a certain fraction of the spins are ‘free’ and are not involved in the ordering. If we assume that Fe substitutes in ZnGa_2O_4 as an alloy with Fe_3O_4 , then the saturation magnetization should be $4 \mu_B/\text{Fe}_3\text{O}_4$. If we take the minimum magnetic saturation value to be the point where the hysteresis loop closes, then for $x = 0.15$, this value is about $1 \mu_B/\text{Fe}_3\text{O}_4$ at 5 K. Therefore, to a good approximation, 25% of the substituted Fe completely participates in the bulk ferrimagnetism.

Figure 5 displays magnetization for $x = 0.15$ as a function of the scaled field (H/T) at three different temperatures, (a) 2 K, (b) 5 K, and (c) 200 K. At the two lower temperatures, hysteretic behaviour is observed. The hysteresis is lost by about 100 K, but even at 200 K, the magnetization as a function of the field indicates long range ordering. The nature of the magnetization loops would suggest superparamagnetic behaviour with a blocking temperature of around 100 K. However, superparamagnetism would imply that plots of M as a function of H/T would collapse onto a single S-shaped trace above the blocking temperature. We do not find this. Figure 5(d) shows the temperature dependence of the magnetic coercivity of $x = 0.15$, which grows almost exponentially as the temperature is lowered. At 5 K, the coercivity is about 250 Oe, to be compared with a value of 420 Oe for Fe_3O_4 [32].

Mössbauer spectra were acquired at room temperature (293 K) for the $x = 0.05$ sample and the $x = 0.15$ sample. For both samples, the isomer shift with respect to Fe metal was 0.32 mm s^{-1} and the quadrupolar splitting was 0.52. Neither sample showed, at 293 K, the six-finger pattern characteristic of magnetic ordering. At 4.2 K, the $x = 0.15$ sample displayed both a doublet corresponding to paramagnetic Fe^{3+} and a six-finger pattern corresponding to magnetically ordered Fe^{3+} . The internal field is between 250 and 510 Oe, consistent with the magnetization data. From the Mössbauer fit to the paramagnetic and ferromagnetic phases at

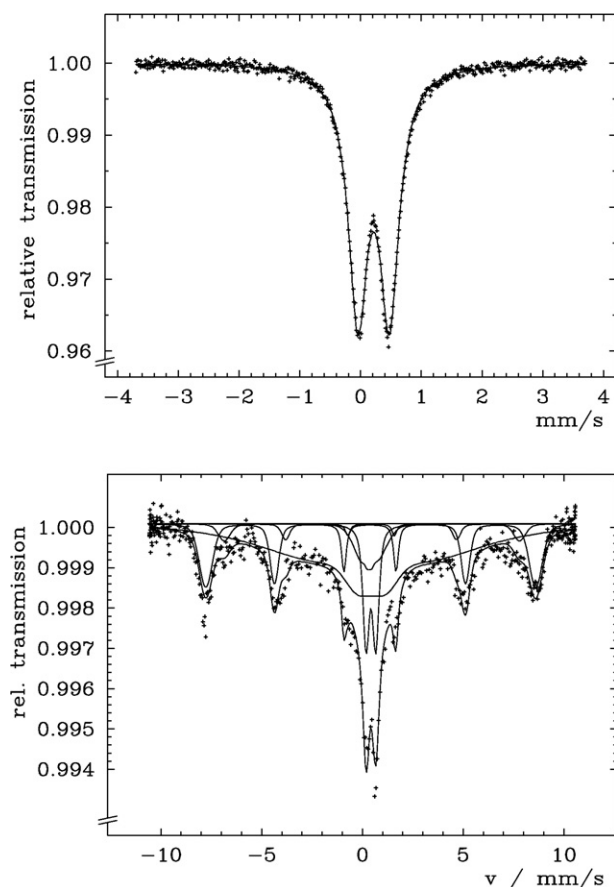


Figure 6. Mössbauer spectra acquired at 293 K (upper panel) and 4.2 K (lower panel) for the nominal $[\text{ZnGa}_2\text{O}_4]_{1-x}[\text{Fe}_3\text{O}_4]_x$ sample with $x = 0.15$.

4.2 K, a relative ratio of 10% (paramagnetic) to 90% (ferromagnetic) was obtained. Mössbauer data and the fit to different components, acquired for the $x = 0.15$ sample, are shown in figure 6. The relative distribution of Fe^{3+} on octahedral and tetrahedral sites could not be obtained from the present set of experiments. Experiments are planned for the future with labelled ^{57}Fe in order to obtain higher resolution data that will allow the Fe ion site selection to be probed.

The title compounds presumably have random substitution of ferric ions on both the tetrahedral and octahedral sites in the semiconducting host spinel structure. Since there are twice as many octahedral sites as there are tetrahedral sites, if the spins behave as they do in bulk Fe_3O_4 , ferromagnetism can ensue. We believe this to lie at the origin of the observed magnetic behaviour. Further Mössbauer studies as well as powder neutron diffraction measurements are planned in order to better characterize the title compounds. Our results suggest that dilute *ferrimagnetic* semiconductors are worthy objects of study.

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