High-temperature ferromagnetism in Cu-doped GaP by SQUID magnetometry and ferromagnetic resonance measurements

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The search for ferromagnetism above room temperature in semiconductors doped with paramagnetic ions has intensified in recent years because of the potential of combining magnetic information storage and electronic switching in one spintronic device. Here we report an observation of ferromagnetism well above room temperature in gallium phosphide doped with Cu^{2+} detected by ferromagnetic resonance and SQUID magnetometry. Other important features of the results *in this p-type Cu-doped GaP* are the high Curie temperature above 700 K significantly higher than previous observations, the relatively simple low-temperature bulk sintering process used to synthesize the material, which will significantly reduce the cost of large-scale production, and the use of copper as the dopant rather than manganese, which precludes ferromagnetic clusters or magnetic alloy impurities as the origin of the ferromagnetism. *Ab initio* calculations also show the existence of ferromagnetism in Cu-doped GaP. When the spin-orbit coupling is included, the total moment is enhanced and we get a total magnetic moment of $0.31\mu_B$ with a local moment on Cu 0.082 and on P $0.204\mu_B$.

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Semiconducting switching elements in logic circuits involve transport of holes or electrons induced at specific voltages. On the other hand, storage of information employs a separate magnetic material in which magnetic-field alignment of micrometer-long and nanometer-wide magnetic particles is the basis of the storage mechanism. In recent years, there has been considerable interest in combining both the storage and transport into one material by developing magnetic semiconductors consisting of alloys of a magnetic ion such as Mn^{2+} and a semiconducting material. These materials have many device applications such as spin valve transistors, spin light emitting diodes, and nonvolatile memory. In such materials, the magnetic-field-induced orientation of the spin of the charge carriers would be the basis of information storage. Ferromagnetism above 173 K has been observed in GaAs doped with manganese, just by controlling its defect structure and the crystallinity.[1] There have also been reports of ferromagnetism above room temperature in GaMnN, GaMnP, and a number of other materials.[2–4] None of these materials were synthesized by a bulk sintering process but rather by such methods as ion implantation. The highest Curie temperature reported to date is above 400 K in manganese-doped zinc oxide.[5] The origin of the ferromagnetism in these alloys is a subject of current research. It has been proposed that the exchange interaction between the dopant spins is mediated by the holes or electrons.[6] In the ferromagnetic state, there is a splitting of the valence and conducting band depending on the spin orientation of the charge carriers. The model predicts that hole-doped semiconductors will have higher Curie temperatures than electron-doped materials.

Manganese may not be the best choice for a dopant. Manganese clusters have been shown to be ferromagnetic, motivating the suggestion that the ferromagnetism observed in the doped semiconductors arises from manganese clusters.[7,8] Also there is the added problem of the possible formation of GaMn and MnP during the synthesis, which are known to be ferromagnetic at high temperatures.[9] In order to circumvent these difficulties, we have chosen copper as the dopant. Cu has a charge of 2+ and will be a hole dopant. There is no evidence of ferromagnetism in bulk copper or copper clusters, as well as no known ferromagnetic alloys such as CuP or GaCu. Copper clusters refer to small nanoparticles of copper embedded in the material. To further support the lack of evidence of ferromagnetism in Cu clusters, we have made magnetic measurements on 25 nm copper nanoparticles obtained from Aldrich. No evidence of ferromagnetism was found in these copper nanoparticles. Further, a number of molecular orbital calculations on Cu_N nanoparticles ranging in size from $N=2$ to 79 do not show the ground state to be ferromagnetic.[10,11] There have been reports of high-temperature ferromagnetism in complexes of copper with organic ligands such as $[Cu_2(S)_2\ (H_2O)]$, where S=N-(2-hydroxybenzyl)-L-alanine.[12] The existence of these kind of ligands in GaP:Cu is highly unlikely. Elemental analysis of our samples by EDS shows only the presence of Ga, P, Cu, and O. GaP has a number of advantages for a potential magnetic semiconductor. It is a component in AlGaInP used in light-emitting diodes and high-speed electronics, and its lattice parameters are close to silicon, perhaps enabling an integration of dilute magnetic semiconductors with conventional silcon circuitry. Here we report SQUID magnetometry and ferromagnetic resonance (FMR) evidence for ferromagnetism well above room temperature in copper-doped gallium phosphide. Important features of the observation are the relatively simple sintering process for making the material and the significantly higher Curie temperature compared to previous observations.

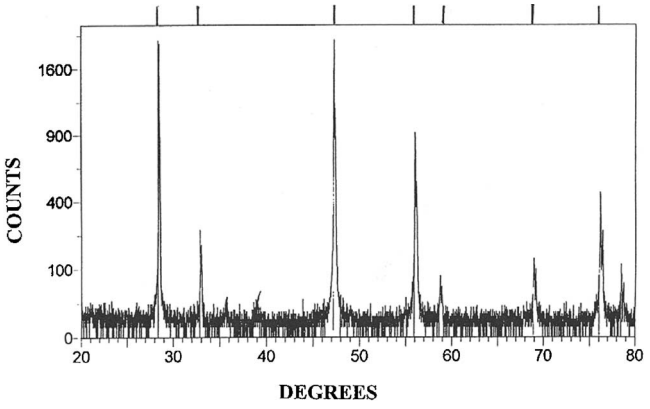

FIG. 1. X-ray diffraction of GaP:Cu. The lines at the top are the positions of pure GaP.

The samples were synthesized by thoroughly mixing in the ratio 0.03 molecular weight of CuO to one molecular weight of 99.999% pure gallium phosphide obtained from Alfa Aesar and then grinding the mixture using a mortar and pestle. The GaP used was examined by electron paramagnetic resonance (EPR) prior to processing to insure no magnetic impurities were present in the material. No evidence for any magnetic impurities were found. EPR is sensitive to magnetic species to one part per ten billion. The samples in the form of pressed pellets contained in an alumina boat were sintered at 500 °C in an oven for 4 h in air followed by rapid quenching to room temperature.The sintered samples were examined by x-ray diffraction employing a Scintag x-ray instrument using the Cu *K* alpha line. Figure 1 shows the powder x-ray-diffraction spectra. The lines at the top of the figure are those expected for pure gallium phosphide. The peaks in the doped sample occur at the same scattering angles as pure GaP and no impurity lines are evident in the data. The sintered samples were also examined by Induction Coil Plasma mass spectrometry (ICP-MS), which showed no magnetic metals at levels above 2 parts per billion. The presence of copper in the samples was, however, detected. Figure 2 shows the Raman spectra of the transverse-optical (TO) mode and the longitudinal-optical (LO) mode in doped and undoped GaP recorded using a JY Horiba confocal Raman spectrometer. The higher-frequency LO mode is downshifted by 3 cm^{-1} in the copper-doped sample. It has been shown in other semiconductors such as GaN that the LO mode is coupled to the plasma mode whose frequency is proportional to the electron carrier concentration.[13] The LO mode has been shown to shift with electron carrier concentration. The observed decrease in the frequency of the LO mode in the Cu-doped GaP indicates a decrease in the electron carrier concentration consistent with hole doping. To further verify this interpretation, we have doped GaP with V^{5+} by a similar sintering process to that described above. It was observed that the LO mode increased by 3 cm^{-1}, consistent with electron doping of the sample.

Samples made with much higher percentages of copper oxide do not show ferromagnetism. If the ferromagnetism were a result of an unknown copper ferromagnetic phase formed during sintering, the ferromagnetic fraction should increase with higher percentages of copper oxide.

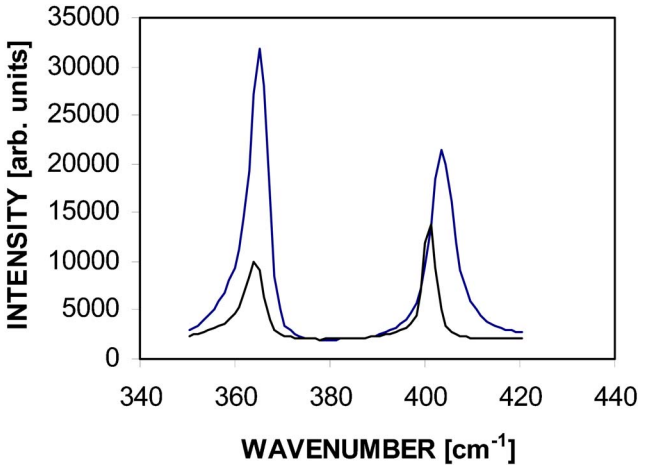

FIG. 2. (Color online) Raman spectrum of TO and LO modes in the undoped and doped (downshifted spectrum) in gallium phosphide.

Figure 3 shows SQUID MPMS2 measurements of the dc magnetic-field dependence of the magnetization at a number of temperatures. The saturation magnetization at 300 K is 1.5×10^{-2} emu/g. This soft magnetic character is typical of dilute magnetic ferromagnets that have low coercivity, and low remnance. Note that the as-obtained magnetic data in Fig. 3 show perfect saturation at room temperature at fields above 3 kOe indicating that there are no additional contributions arising from any diamagnetic species or paramagnetic term arising from possible unreacted CuO, which is antiferromagnetic well below room temperature. Furthermore, below 50 K the magnetization does show an additional "paramagnetic-like" contribution that increases with decreasing temperatures. This is a well known common feature in the temperature dependence of the magnetization of all dilute magnetic semiconductors, which may be related to the defect

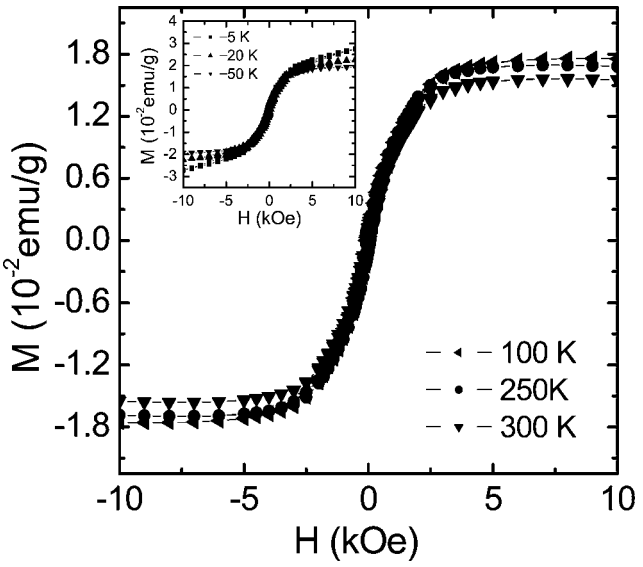

FIG. 3. Magnetic hysteretic loops at various temperatures for GaP doped with 3 wt. % Cu. The inset with the loops below 100 K showing the additional "paramagnetic-like" contribution increasing with decreasing temperatures typical for DMS materials.

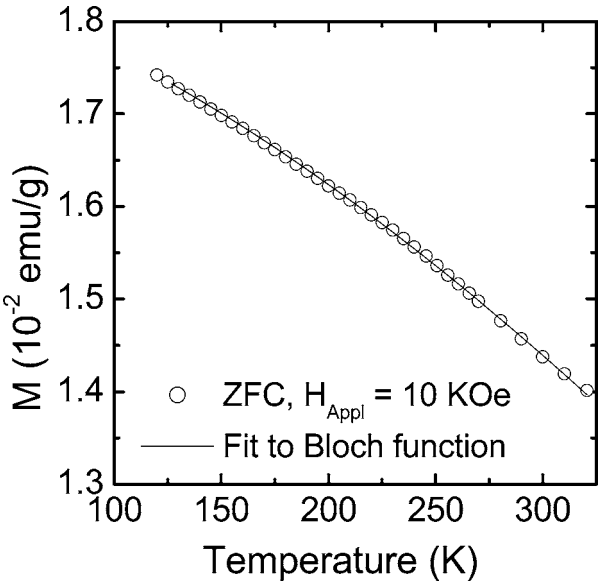

FIG. 4. Temperature dependence of the magnetization. The line through the data is the best fit to the Bloch equation [Eq. (1)].

structure in the material. The coercivity at room temperature is 125 Oe. Figure 4 is the temperature dependence of the magnetization at 10 KOe. The line through the data is a fit to the Bloch equation,

$$M(T) = M(0)(1 - AT^{3/2}) \tag{1}$$

for $A = 4.0 \times 10^{-5}$ K$^{-3/2}$ and $M(0) = 18.44$ memu/g.

The observed $T^{3/2}$ behavior is exactly what is expected from Bloch spin wave theory for low spin excitations in an ordered system. Such a fit over a wide temperature range in excess of 200 K is indeed remarkable. Figure 5 is a plot of the temperature dependence of the coercivity. The line through the data is a fit to the exponential decay.

$$H_c = H_{co} + B \exp(-T/C). \tag{2}$$

For $H_{co} = 298.38$ Oe, $B = 137.07$ Oe and $C = 728.97$ K. This exponential dependence of coercivity is expected from an

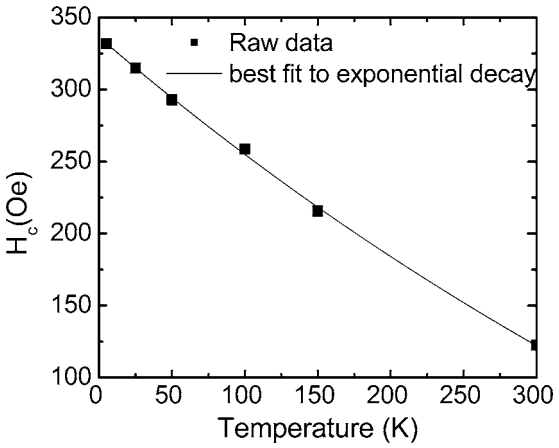

FIG. 5. Temperature dependence of the coercivity. The line through the data is a fit to an exponential decay [Eq. (2)].

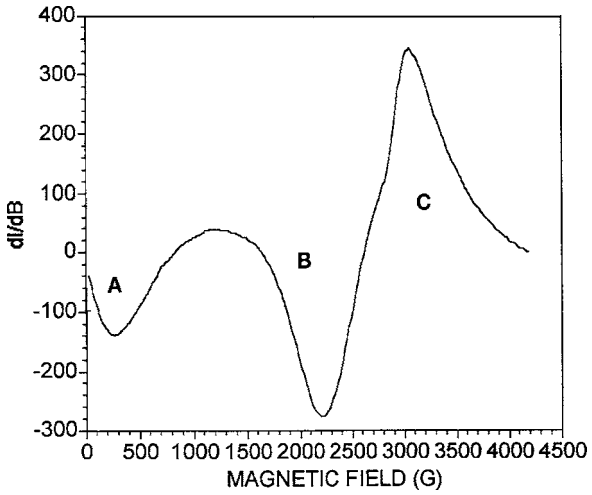

FIG. 6. Ferromagnetic resonance spectrum, derivative of the absorption I with respect to B, recorded at room temperature. Absorption A is the low-field nonresonant absorption, which exists in the ferromagnetic state. Line B is the ferromagnetic resonance absorption. Line C is likely from some unreacted CuO in sample.

activation process in magnetic systems. The above characteristics of $M(T)$ and $H_c(T)$ rules out any additional contribution to magnetism that could arise from small clusters or other possible magnetic phases. Furthermore, a low-field temperature dependence of the magnetization in the field-cooled and zero-field-cooled states would easily show the existence of any possible blocking phenomenon or some type of spin freezing process that would arise from clusters and other such magnetic nanoscale entities. We have no evidence for the above in our samples. What we observe is a robust ferromagnetism above 70 K even satisfying the Bloch spin wave theory over a wide temperature range indicating a rather high magnetic transition temperature.

The samples have also been examined by ferromagnetic resonance (FMR), which is a highly sensitive method for verifying the existence of ferromagnetism.[14] The temperature of the sample was controlled by flowing heated or cold nitrogen gas through a doubled-walled quartz tube that is part of an ADP Heli-Tran system, and which is inserted through the center of the microwave cavity. The powder sample was contained in the quartz tube and located at the center of the microwave cavity, which is located at the center between the poles of an electromagnet. Figure 6 shows the FMR spectrum at 300 K recorded using a Varian E-9 spectrometer operating at 9.2 GHz. Three lines are evident in the spectrum: a low-field nonresonant signal (A), a ferromagnetic resonance signal (B), and a component (C), which is likely due to some unreacted CuO in the sample. In a single crystal, the magnetic-field position of the FMR signal depends on the orientation of the dc magnetic field with respect to important symmetry directions in the unit cell. The spectra shown here are from a collection of randomly oriented grains and are powder patterns representing the sum of spectra from all orientations of the dc magnetic field. It should be noted that CuO is not ferromagnetic and cannot be the source of the ferromagnetism observed here.[15] The presence of the low-field nonresonant absorption signal is a well established in-

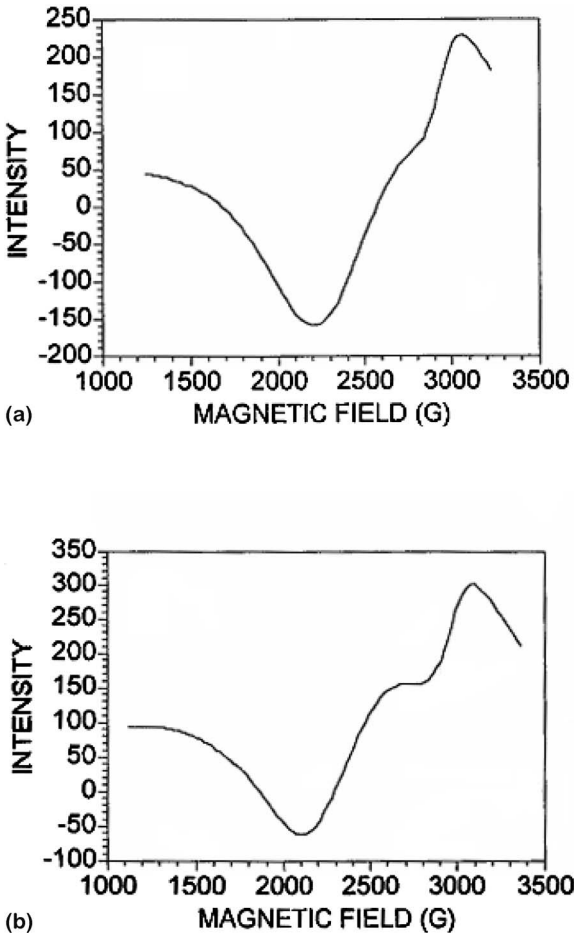

FIG. 7. Ferromagnetic resonance at (a) 300 K and (b) 138 K showing the shift of the FMR resonance to lower fields at lower temperature.

dication of ferromagnetism in materials.[16,17] The signal occurs because the permeability in the ferromagnetic state depends on the applied magnetic field increasing at low fields to a maximum and then decreasing. Since the surface resistance depends on the square root of the permeability, the microwave absorption depends nonlinearly on the strength of the dc magnetic field resulting in a nonresonant derivative signal centered at zero field. This signal is not present in the paramagnetic state and emerges as the temperature is lowered to below T_c. We have been able to observe the low-field nonresonant absorption at temperatures as high as 524 K, the upper limit of our temperature apparatus in the resonance experiment. The characteristic distinguishing FMR signals from EPR signals is a strong temperature dependence of the field position and linewidth of the resonance. Figure 7 shows the FMR spectra at 300 K (a) and at 118 K (b) showing the large shift to lower dc magnetic field at low temperature. Figure 8 gives the temperature dependence of the field position of the line above room temperature, showing that the material is still ferromagnetic at 524 K. The spectrum labeled *C* does not display this temperature-dependent behavior and is not a ferromagnetic resonance signal. Above the Curie temperature, the FMR signal becomes an EPR signal of Cu^{+2} having a field position independent of temperature

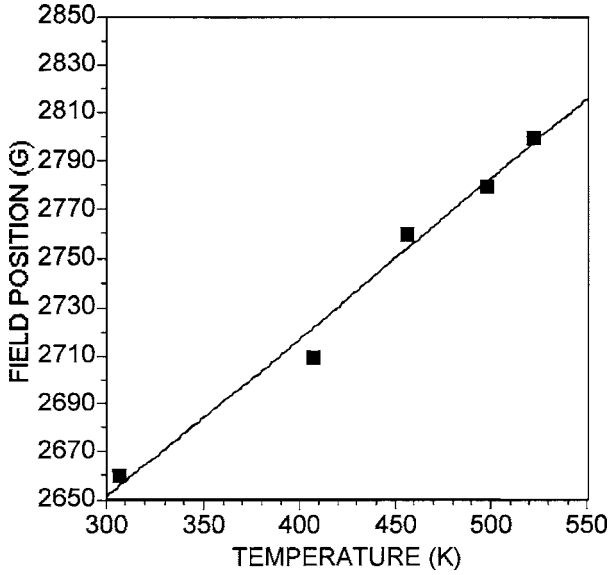

FIG. 8. Temperature dependence of field position of ferromagnetic resonance above room temperature.

corresponding to that of spectra *C* in Fig. 6, which is 2940 G. Extrapolating the data in Fig. 8 to this value allows an estimate of T_c of 739 K, which is in reasonable agreement with the estimate from the temperature dependence of the magnetization. These results, both the SQUID and FMR measurements, have been repeated in many samples and in GaP obtained from different sources.

In order to study the magnetic properties, we have also performed the total energy calculations for $Cu_{0.03}Ga_{0.97}P$ using the projector augmented-wave (PAW) method as invoked by the VASP program package. The parametrization for the exchange and correlation potential proposed by Ceperly and Alder (CA) was employed. In the present calculations, we made use of PAW potentials that valence states 3*d* and 4*s* for Cu, 3*d* and 4*s* for Ga, and 3*s* and 3*p* for P. The kinetic-energy cutoff was 600 eV. The optimization of the geometry has been done using the Hellmann-Feynman forces on the atoms and stresses on the supercell for each volume. For sampling the irreducible wedge of the Brillouin zone, we used *k*-point grids of $4\times4\times2$ for the geometry optimization and $8\times8\times4$ for the electronic-structure calculation at the equilibrium volume. More details about the calculations method can be found in Ref. 5.

Our calculated magnetic moments are shown in Table I. The calculated total moment without spin-orbit coupling is $0.027\mu_B$ and the local magnetic moment of Cu is $0.007\mu_B$ and P is $0.019\mu_B$. When the spin-orbit coupling is included,

TABLE I. Calculated magnetic moments (in μ_B) for $Cu_{0.03}Ga_{0.97}P$.

	μ_{cell}	μ_{Cu}	μ_P
Without spin orbit	0.027	0.007	0.019
With spin orbit	0.310	0.082	0.204

the total moment increased to a total magnetic moment of $0.31\mu_B$ with a local moment on Cu 0.082 and on P $0.204\mu_B$. So spin-orbit coupling is very important. It is interesting to note that on the P site, there is a significantly large moment. This is due to the large splitting of p bands of P induced by Cu doping.

In summary, we have presented clear evidence from SQUID magnetometry, ferromagnetic resonance, and Raman spectrometry measurements that copper-doped gallium phosphide made by a simple sintering process is ferromagnetic at temperatures much higher than any previously reported dilute magnetic semiconductor. Our *ab initio* calculations support the existence of ferromagnetism in this system.

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