Effect of carbon doping on electronic transitions in Mn$_5$Ge$_3$

N. Stojilovic,1,a) S. V. Dordevic,2 Rongwei Hu,3,b) and C. Petrovic3

1Department of Physics and Astronomy, University of Wisconsin Oshkosh, Oshkosh, Wisconsin 54901, USA
2Department of Physics, The University of Akron, Akron, Ohio 44325, USA
3Brookhaven National Laboratory, Condensed Matter Physics and Materials Science Department, Upton, New York 11973, USA

(Received 19 June 2013; accepted 18 July 2013; published online 5 August 2013)

Mn$_5$Ge$_3$ is a ferromagnetic compound with high Curie temperature ($T_c = 293$ K), high spin polarization, and a good lattice match to germanium. Doping Mn$_5$Ge$_3$ with carbon increases $T_c$ above room temperature and makes these compounds promising candidates for spin injectors for potential spintronics applications. The resistivity and magnetic susceptibility measurements show anisotropic behavior of these compounds. Optical spectroscopy is employed to measure near-normal reflectance of Mn$_5$Ge$_3$C$_{0.89}$ in the frequency range from far-infrared to ultraviolet at three different temperatures (10, 200, and 300 K), and results are compared with those on pure Mn$_5$Ge$_3$. Both Mn$_5$Ge$_3$ and Mn$_5$Ge$_3$C$_{0.89}$ have weak temperature dependence of the optical properties in the 10–300 K range, and both have similar electrodynamics responses with similar temperature trends. However, important differences in the region of interband transitions, indicating the electronic nature of the increased ferromagnetic stability of carbon doped compound, are observed. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4817429]

I. INTRODUCTION

Almost 30 years ago, De Groot and collaborators theoretically predicted the existence of a novel type of magnetic materials—half-metallic ferromagnets (HMFM).1 These new materials exhibit an unusual property: one spin direction is metallic and the other one is semiconducting. Band structure calculations indicated that all electrons at the Fermi level have the same spin orientation, resulting in a spin-polarized ferromagnetic state (ideal case). Electrons of the opposite spin have a gap in their density of states at the Fermi level and take no part in conduction. The unusual electronic structure of HMFM needs to be analyzed taking into account correlation effects such as electron-magnon coupling.2 The appearance of nonquasiparticle (incoherent) states in the energy gap near the Fermi level is correlation effect characteristic for HMFM. The origin of these states is connected with spin-polaron processes.3 Half-metallicity can be suppressed by defects, spin-orbit coupling, and increased temperature. For example, thermal fluctuations at finite temperatures can induce mixing of spin up and spin down states at the Fermi level. In addition, scattering on defects can randomize spins.

Spin injection from a ferromagnetic metal into a semiconductor is practically impossible due to the large lattice and conductivity mismatch between a metal and a semiconductor. Therefore, for spintronics applications, finding a compound that can be incorporated into the mainstream semiconductors, such as silicon or germanium, is crucial and Mn$_5$Ge$_3$–based compounds are excellent candidates. Based on point-contact Andreev reflection experiments Mn$_5$Ge$_3$ was found to have spin polarization in the 43%–54% range.4

The degree of spin polarization of band carriers is a crucial parameter. Also, because of a good lattice match to germanium, Mn$_5$Ge$_3$ is now being considered for use in spintronics applications.4 However, pure Mn$_5$Ge$_3$ has $T_c = 293$ K,5 which is still low for technological applications. The increase in both spin polarization and Curie temperature (above room temperature) in Fe-doped Mn$_5$Ge$_3$ was reported by Chen et al.6 Gajdzik et al. reported the enhanced ferromagnetic stability in connection with the lattice compression which was interpreted in terms of Mn-Mn interaction mediated by C based on a change in the electronic structure.7 The increased $T_c$ in Mn$_5$Ge$_3$C$_x$ compounds was also confirmed in a study based on first principles and Monte Carlo simulations where the effect was proposed to be of electronic nature while the structural distortions were a secondary effect.8 The high Curie temperature can compensate for lower value of polarization. Also, high spin-polarized injection efficiency is more important than 100% spin polarization.

In our earlier study we used infrared spectroscopy to probe pure Mn$_5$Ge$_3$ compound.9 In this study we probe the electrodynamical response of Mn$_5$Ge$_3$C$_{0.89}$ ($T_c = 305$ K) by means of optical spectroscopy in the frequency range from far-infrared to ultraviolet (70–50,000 cm$^{-1}$) at various temperatures, and compare the results primarily with those on pure Mn$_5$Ge$_3$.9 We also look at similarities and differences between the optical spectra of Mn$_5$Ge$_3$C$_x$-based compounds and other related materials such as CrO$_2$,10 NiMnSb,11 La$_{1-x}$Sr$_x$MnO$_3$,12 and La$_{0.67}$Ca$_{0.33}$MnO$_3$.13

II. EXPERIMENTAL DETAILS

Electrical transport and magnetization measurements were carried out in Quantum Design PPMS-9 and MPMS-XL5. The technique for measurements of the near-normal reflectance of sub-millimeter sized samples was first employed
by Homes et al.\textsuperscript{14} In brief, the sample is placed at the focus of light beam, with the beam size exceeding that of the sample, allowing its entire area to be probed. The sample and the reference mirror are mounted on the nonreflecting cones. Rotation of the cryostat by 90° using mechanical stops allows easy and quick sample-mirror exchange. Using the sample as its own reference and evaporation of materials whose reflectance is known (gold or aluminum) corrects for the scattering effects caused by the surface microstructure. Coating is thin enough to preserve the microstructure of the sample and thick enough to be greater than the penetration depth in the frequency region of interest. The size of the samples measured in this study was about 1 mm × 1 mm. The hexagonal Mn$_5$Ge$_3$ (space group P6$_3$/mcm) has two Mn sublattices (Mn$_I$ and Mn$_II$) with different coordination. Mn$_5$Ge$_3$C$_x$ has similar structure with carbon atoms taking interstitial sites at the center of Mn$_II$ octahedron, modifying the 3$d$-states of Mn$_II$ and leaving the Mn$_I$ states almost unaffected.\textsuperscript{8} IR reflectance measurements were performed on a Bruker IFS 66v/s system, whereas UV-vis experiments were performed using Varian/Cary 300. The optical constants were extracted using Kramers–Kronig (KK) analysis which is model-independent and preserves spectral information from the measured reflectivity.

III. RESULTS AND DISCUSSIONS

Figure 1 displays the temperature dependence of the in-plane, $\rho_a(T)$, and out-of-plane, $\rho_c(T)$, resistivity for temperatures up to 300 K. A considerable change in the resistivity can be seen at the Curie temperature and anisotropic transport properties of Mn$_5$Ge$_3$. In particular, the values of $\rho_c(T)$ are greater than those for $\rho_a(T)$ in the temperature range studied. The ratio $\rho_c(T)/\rho_a(T)$ varies between 1.04 and 1.40. Also, $\rho_c(300\,\text{K})/\rho_a(4\,\text{K}) = 3.2$ and $\rho_c(300\,\text{K})/\rho_a(4\,\text{K}) = 2.7$. The resistivity values at 4 K are $\rho_c(4\,\text{K}) = 108.6\,\mu\Omega\text{cm}$ and $\rho_a(4\,\text{K}) = 86.3\,\mu\Omega\text{cm}$. Magnetization as a function of the H-field is displayed in Figure 2 with the variation of the magnetic susceptibility, $\chi = M/H$, as a function of temperature for in-plane and out-of-plane H-field.

Near-normal reflectance in a wide frequency range (70–50,000 cm$^{-1}$) has been used to probe electronic structure of Mn$_5$Ge$_3$ and Mn$_5$Ge$_3$C$_{0.89}$ at 10, 200, and 300 K, and results are displayed in Figure 3. Although reflectance of $\chi = M/H$, with temperature shown as an inset. Although the direction perpendicular to the surface is a hard axis the anisotropy in magnetization is not very significant. A peak in magnetic susceptibility is associated with the Curie temperature, below which magnetic susceptibility exhibits significant anisotropy.

![FIG. 1.](image1.png) FIG. 1. The in-plane, $\rho_a$ (squares), and out-of-plane, $\rho_c$ (circles), resistivity for temperatures up to 300 K and in zero field.

![FIG. 2.](image2.png) FIG. 2. Magnetization versus H-field. The inset shows the magnetic susceptibility, $\chi = M/H$, as a function of temperature for in-plane and out-of-plane H-field.

![FIG. 3.](image3.png) FIG. 3. Reflectance of Mn$_5$Ge$_3$ (a) and Mn$_5$Ge$_3$C$_{0.89}$ (b), at 10 (blue), 200 (green), and 300 K (red). The temperature dependence of both compounds is most notable below about 1500 cm$^{-1}$. Both spectra show some characteristics of metallic behavior and the effects of carbon doping are most notable at higher frequencies.
The temperature dependence of reflectance for both samples is weak and is limited to the region below 1500 cm\(^{-1}\). There are no sharp features in the infrared region that would indicate optical phonons as it was observed in some other HMFMs.\(^\text{10,13}\) The optical phonon modes are screened in the metallic phase at temperatures below \(T_C\), consistent with the optical study of a La\(_{0.67}\)Ca\(_{0.33}\)MnO\(_3\) HMF single crystal.\(^\text{13}\) The differences between pure and C-doped Mn\(_5\)Ge\(_3\) are small in the infrared region of the spectrum, but are quite significant above 10 000 cm\(^{-1}\), in the region where interband transitions occur. In particular, carbon doping decreases the reflectivity of Mn\(_5\)Ge\(_3\) above 10 000 cm\(^{-1}\). The reflectance of Mn\(_5\)Ge\(_3\)C\(_{0.89}\) is lower than that of Mn\(_5\)Ge\(_3\) in the 10 000–41 000 cm\(^{-1}\) spectral range and larger above 41 000 cm\(^{-1}\). The maximum difference in reflectance is about 10%.

The structures resulting from the interband transitions are usually visible in the optical conductivity data. The complex optical conductivity, \(\sigma(\omega) = \sigma_1(\omega) + i \sigma_2(\omega)\), is extracted from measured reflectance using KK analysis and a Hagen-Rubens low-frequency extrapolation. Figure 4 shows the real part of optical conductivity \(\sigma_1(\omega)\) of Mn\(_5\)Ge\(_3\) (Fig. 4(a)) and Mn\(_5\)Ge\(_3\)C\(_{0.89}\) (Fig. 4(b)). Some general characteristics of metallic behavior are evident, such as a Drude-like mode at low frequencies. However, there are some deviations from metallic behavior as well. One can identify three contributions to \(\sigma_1(\omega)\): (i) a Drude-like peak at zero frequency, which narrows as temperature decreases, (ii) a region of relatively constant conductivity (between about 1000 and 10 000 cm\(^{-1}\)), and (iii) a region of interband transitions above 10 000 cm\(^{-1}\) where the pure and C-doped Mn\(_5\)Ge\(_3\) show significant differences. More details on these contributions are given in our earlier study on pure Mn\(_5\)Ge\(_3\).\(^\text{9}\) The temperature dependence of the real part of the optical conductivity is limited to the region below 3000 cm\(^{-1}\), indicating characteristic energy scale responsible for the changes in the electronic structure. This frequency range is notably smaller than the one reported in another HMFMs La\(_{1−x}\)Sr\(_x\) MnO\(_3\).\(^\text{12}\) At lower frequencies, optical conductivity increases with decreasing temperature, accompanied by narrowing of the Drude-like peak for both compounds. This narrowing of the Drude-like peak with decreasing temperature is slightly more pronounced in the carbon-doped compound. In the frequency region between 900 and 2000 cm\(^{-1}\) the temperature dependence of optical conductivity is reversed. In a related study of C-ion implementation into Mn\(_5\)Ge\(_3\), temperature dependence of electrical resistivity was investigated and metallic behavior similar to Mn\(_5\)Ge\(_3\) was observed,\(^\text{15}\) consistent with our optical reflectance spectroscopy experiments. A broad and featureless optical conductivity in wide frequency region is a result of interband transitions. For instance, coupling to magnetic resonances or particular excitations may produce side bands that form a broad incoherent background in the optical conductivity data.\(^\text{16}\) The spectral weight lost from the Drude peak, observed in the optical conductivity data, is gained at higher temperatures in the 600–2000 cm\(^{-1}\) region. This explains the temperature trend inversion in this frequency range, which is more pronounced in pure than in carbon doped compound.

To gain deeper insight into the electronic properties of Mn\(_5\)Ge\(_3\) and Mn\(_5\)Ge\(_3\)C\(_{0.89}\) compounds we first employ the so-called “one-component approach” which is based on a single type of carriers whose scattering rate depends on frequency.\(^\text{17}\) Within this approach one uses the extended Drude model to calculate the optical scattering rate \(1/\tau(\omega)\) and effective mass \(m^* (\omega) \approx m_0\) from the optical conductivity \(\sigma(\omega)\) as \(1/\tau(\omega) = (\omega^2/4\pi)\text{Re}(1/\sigma(\omega))\) and \(m^* (\omega) \approx m_0 = (\omega^2/4\pi)\text{Im}(1/\sigma(\omega))/\omega\), respectively. Here, \(\omega_p\) is the plasma frequency and is related to the carrier density \(n\) and their band mass \(m_b\) via \(\omega_p = 4\pi e^2 n/m_b\). The plasma frequency is estimated after integrating \(\sigma_1(\omega)\) from zero frequency up to a cut-off frequency \(\omega_c\) coinciding with the onset of the electronic interband transitions. In particular, \(\omega^2_p\) is obtained by integrating optical conductivity up to 10 000 cm\(^{-1}\) (\(\omega_p = 33 000\) cm\(^{-1}\) and 32 320 cm\(^{-1}\) for Mn\(_5\)Ge\(_3\) and Mn\(_5\)Ge\(_3\)C\(_{0.89}\), respectively). However, the value of plasma frequency obtained in this way slightly depends on the choice of the cut-off frequency. For example, integration of optical conductivity up to frequencies 1000 cm\(^{-1}\) lower or higher than the selected frequency changes the value of \(\omega_p\) by 1%.

The scattering rates of pure and carbon-doped Mn\(_5\)Ge\(_3\) compounds are displayed in Figs. 5(a) and 5(b), respectively. At low frequencies (<1500 cm\(^{-1}\)) scattering rates exhibit decrease with decreasing temperature, consistent with the DC transport. The strong frequency dependence of the scattering rate indicates that the intraband response deviates from the simple Drude behavior, in agreement with the behavior observed on NiMnSb,\(^\text{11}\) another HMFMs.
comparison of the two compounds reveal that the scattering rate of carbon-doped Mn$_5$Ge$_3$ is slightly greater, which is expected from the compound with increased disorder for the three temperatures studied, and has a sharper drop below 250 cm$^{-1}$. In the 600–2000 cm$^{-1}$ region we see the trend inversion, which is more pronounced in pure than in carbon doped compound, consistent with optical conductivity results. The scattering rate is greater than $\omega$, which is in disagreement with the Fermi-liquid (FL) behavior that has been observed on NiMnSb. It is known that nonquasiparticle states in HMFM are not described by the FL theory. Also, the quadratic form of the scattering rate, expected for electron-electron scattering of a Fermi liquid, is not present here. In a number of strongly correlated systems disorder can lead to non-Fermi liquid behavior and may play a role in this case as well. Optical scattering rates obey power laws which may imply coupling of charge carriers to bosonic modes of magnetic origin. Also, a threshold in the scattering rate at about 90 meV observed in a related study on NiMnSb is absent in our compounds. The threshold in the scattering rate can be connected with the absence of spin-flip carrier scattering below the threshold value, indicating a highly spin polarized system. Therefore, the absence of a threshold in the scattering rate in Mn$_5$Ge$_3$ and C-doped Mn$_5$Ge$_3$ leaves the possibility of spin-flip carrier scattering in these compounds. The spin-flip occurrence can be due to scattering by magnons or magnetic impurities. The absence of the flat region in $1/\tau(\omega)$ spectra at low frequencies is consistent with partial spin polarization.

The narrow Drude resonance, developing at low temperatures in $\sigma(\omega)$ is well represented by the quasiparticle effective mass. Figs. 6(a) and 6(b) display effective mass $m^*/m_0$ for pure and C-doped Mn$_5$Ge$_3$, respectively. Correlation effects are expected to produce mass enhancement. In addition, electron-boson interactions can result in the increase of the effective mass at low energies and the value of effective mass as $\omega \rightarrow 0$ is related to the quasiparticle renormalization amplitude. The effective mass for C-doped sample is slightly greater at lowest frequencies at 10 K and 200 K but smaller at 300 K which is the signature of correlation effects at low temperatures. The increase in the quasiparticle effective mass is accompanied with the decrease in the scattering rate.

Since no clear peaks characteristic of transitions between bands were visible in the optical conductivity data, the closer look on the reflectivity measurements is taken. Figure 7 displays the reflectivity of Mn$_5$Ge$_3$ and Mn$_5$Ge$_3$C$_{0.89}$ at 10 K along with their corresponding Drude-Lorentz (DL) fits. The minimal models to obtain good fits involve one Drude ($D$) and two Lorentz modes ($L_1$ and $L_2$) for each compound. The parameters used to obtain fits are summarized in Table I. The oscillator at 18 000 cm$^{-1}$ (22.587 cm$^{-1}$) for pure (doped) compound reflects the effect of interband transitions whereas the oscillator at 1480 cm$^{-1}$ (1294 cm$^{-1}$) seems to indicate the presence of low-lying transition and we cautiously associate it with excitations across the spin-flip gap. Doping with carbon shifts the oscillator from 1480 cm$^{-1}$ to 1294 cm$^{-1}$ indicating decrease in the spin-flip gap. $L_2$ mode of Mn$_5$Ge$_3$C$_{0.89}$ has smaller strength and the peak is shifted by about 4500 cm$^{-1}$ toward higher frequencies. Although the doping with carbon compresses the lattice, it also has a clear signature in the region of interband transitions, indicating the electronic nature of the increased $T_C$, consistent with the first principle calculations. Also, the hybridization of the Mn$_{II}$ 3$d$-states and C 2$p$-states leads to an increase in the density of
states at the Fermi level in both spin channels. The optical reflectance measurements proved to be a sensitive tool in probing interband transitions in this class of compounds.

IV. CONCLUSIONS

In summary, optical reflectance spectroscopy was used to probe electronic properties of Mn$_5$Ge$_3$ and Mn$_5$Ge$_3$C$_{0.89}$ in a wide frequency range (70–50,000 cm$^{-1}$). Both transport and magnetic properties of these compounds exhibit anisotropy. The reflectance of pure and C-doped Mn$_5$Ge$_3$ decreases with increasing frequency and temperature, showing some metallic characteristics. However, reflectance of both compounds shows relatively small temperature dependence. The differences between the two compounds are most significant in the region of interband transitions. This indicated that the changes due to doping are electronic in nature. Collapse in the scattering rate observed at $\omega < 1000$ cm$^{-1}$ is very likely the result of the coupling of charge carriers to bosonic modes of magnetic origin and the spin-flip gap of approximately 1500 cm$^{-1}$ was observed. Suppression of the relaxation mechanisms at low frequencies appears to be a feature of half-metallic ferromagnet, attributed to its unusual electronic structure. A threshold increase in $1/\tau(\omega)$ observed in CrO$_2$ and NiMnSb is absent in Mn$_5$Ge$_3$ and Mn$_5$Ge$_3$C$_{0.89}$, leaving the possibility of spin-flip carrier scattering in our compounds. The spin-flip occurrence can be due to scattering by magnons or magnetic impurities and doping with carbon decreases the spin-flip gap. The strong frequency dependence of the scattering rate reveals a departure from simple Drude behavior in the region of intraband transitions. Non-Fermi liquid behavior might be the result of strong electronic correlations present in these compounds.

ACKNOWLEDGMENTS

We thank Dr. R. D. Ramsier for the access to his FTIR system. Part of this work is supported by U.S. Department of Energy (Grant No. DE-AC02-98CH10886). N.S. acknowledges UW Oshkosh Faculty Development grant.
