2007

Significant suppression of ferromagnetism by hydrostatic pressure in the diluted magnetic semiconductor Sb2−xVxTe3 with x≈0.03

Jeffrey Dyck
John Carroll University, jdyck@jcu.edu

T J. Mitchell

A J. Luciana

P. C. Quayle

Č. Drašar

See next page for additional authors

Authors
Jeffrey Dyck, T J. Mitchell, A J. Luciana, P. C. Quayle, Č. Drašar, and P. Lošťák

Significant suppression of ferromagnetism by hydrostatic pressure in the diluted magnetic semiconductor $Sb_{2-x}V_xTe_3$ with $x \leqslant 0.03$

J. S. Dyck,[a] T. J. Mitchell, A. J. Luciana, and P. C. Quayle
Department of Physics, John Carroll University, University Heights, Ohio 44118, USA

Č. Drašar and P. Lošťák
Faculty of Chemical Technology, University of Pardubice, 532 10 Pardubice, Czech Republic

(Received 30 July 2007; accepted 31 August 2007; published online 20 September 2007)

The authors report on the hydrostatic pressure dependence of the magnetotransport properties of ferromagnetic $Sb_{2-x}V_xTe_3$ single crystals with $x=0.02-0.03$. Pressure significantly increases the free hole concentration in these compounds. In turn, the Curie temperature is suppressed by roughly 40%, which goes against many models that would predict an increase in Curie temperature with increasing carrier concentration. These results indicate that the ferromagnetism in these materials is carrier mediated and that a full Ruderman-Kittel-Kasuya-Yosida model that takes into account the oscillatory nature of the indirect exchange interaction among localized spins is needed in order to explain the data. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2787881]

The tetradymite-type, narrow-gap semiconductors doped with small concentrations of transition metal ions have been identified as diluted magnetic semiconductors (DMSs).[1–4] In $Sb_{2-x}TM_xTe_3$ single crystals with TM=V,Cr, ferromagnetic order develops at low temperatures (up to ~25 K) with a Curie temperature T_C that is proportional to x.[1,3] The origin of the ferromagnetic order in these materials is so far not established, but a carrier-mediated interaction among localized transition metal (TM) moments is likely given the dilute nature. Theoretical studies have been aimed at predicting T_C in DMS materials and understanding the details of the spin-carrier interactions that give rise to long range ferromagnetic order. (See Ref. 5 for a review.)

Unlike the traditional III-V based diluted magnetic semiconductors doped with manganese where Mn is an acceptor,[6] providing both holes as well as localized spins, the TM ions in Sb_2Te_3 do not alter the background hole concentration p. DMS systems that allow one to independently vary the magnetic ion and free carrier concentration independently are attractive to help study the origin of ferromagnetism in these compounds. Normally, one is faced with the complication of codoping to alter p, introducing a fourth element such as in $(Ga,Be)_{1-x}Mn_xAs$ (Ref. 7) or $(Sb,Bi)_{2-x}V_xTe_3$ (Ref. 8) and in such materials, it is difficult to control x and p simultaneously over a wide series of samples.

This paper is focused on studying the free hole concentration dependence of the Curie temperature by varying p in a single sample using pressure as an external variable. There are very few experiments in the literature utilizing pressure as a tool to investigate spin-carrier interactions in a ferromagnetic DMS. In one very recent example, it was observed that application of high pressures increases T_C from 7.0 to 8.8 K in $In_{1-x}Mn_xSb$ thin films.[9] Unlike in our experiments, pressure did not affect the carrier concentration in $In_{1-x}Mn_xSb$. Therefore, our material system provides a unique opportunity to probe the impact that hole concentration has on the magnetic phase diagram.

Pure Sb_2Te_3 single crystals, the host structure of the DMS considered here, typically have a background hole concentration of 1×10^{20} cm^{-3} due to the presence of native antisite defects. The valence band is sixfold degenerate, and data from the Shubnikov–de Haas measurements suggest the existence of a high mobility upper valence band and a lower valence band with much lower mobility,[10] though the lower valence band is not well characterized. High pressure significantly alters the electrical transport properties in Sb_2Te_3 as evidenced by a decrease in electrical resistivity,[11] an effect also seen in vanadium-doped variants to be presented here. The origin of this change may be due to a modification of the band structure, though recent band structure calculations predict very little change in the valence band near the Fermi energy under hydrostatic pressure.[12] Another possibility is an increase in total hole concentration. First-principles calculations found that hydrostatic pressure lowers the formation energy of antisite defects in Sb_2Te_3,[13] though the kinetics of defect formation has not been studied. Regardless of the mechanism, our high pressure studies demonstrate a clear connection between hole concentration and Curie temperature in vanadium-doped Sb_2Te_3.

Bulk, single crystals of $Sb_{2-x}V_xTe_3$ with $0.02 \leqslant x \leqslant 0.03$ were prepared by a modified Bridgman method. Crystal composition and stoichiometry were verified by atomic absorption spectroscopy and electron probe microanalysis. Samples for magnetotransport measurements under high pressure were cut using a spark erosion technique. The specimens were loaded into a liquid-clamp pressure cell with 3M™ Fluorinert™ electronic liquid FC-77 as pressure transmitting fluid, and pressures were determined *in situ* using a calibrated InSb gauge. Temperature dependent electrical resistivity, Hall effect, and magnetoresistance in a standard six-probe configuration were performed in a 6 T magnet cryostat system using a digital lock-in amplifier operating at 16 Hz. Magnetic field was oriented parallel to the crystallographic c axis. The Hall coefficient was determined from the slope of the Hall resistivity versus field curve, which was linear above 0.5 T for all samples and temperatures (near and below T_C, a small nonlinearity at low fields results from the anomalous Hall effect).

[a]Electronic mail: jdyck@jcu.edu

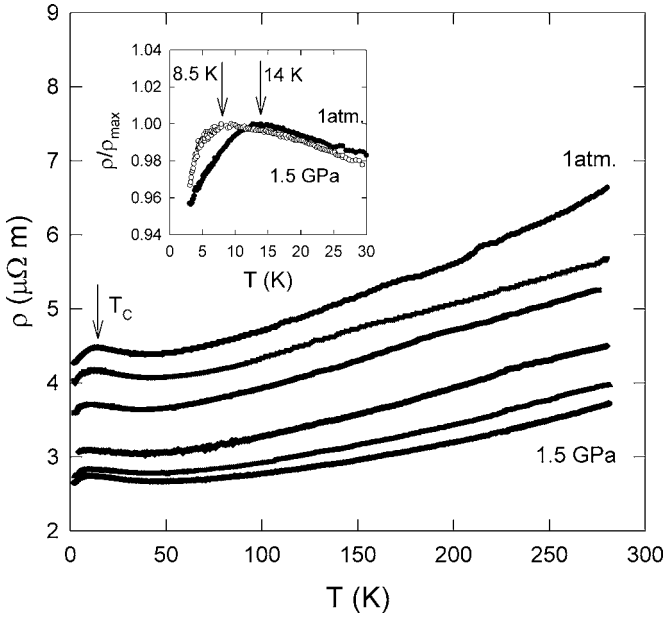

FIG. 1. Pressure dependence of the resistivity vs temperature for $Sb_{1.97}V_{0.03}Te_3$ single crystal. (Inset) Normalized resistivity at low temperature which shows that pressure decreases the Curie temperature.

A plot of resistivity ρ versus temperature for a single crystal of $Sb_{2-x}V_xTe_3$ with $x=0.03$ is given in Fig. 1 for a range of pressures up to 1.5 GPa. Over most of the temperature range, ρ increases with T, characteristic of a degenerately doped semiconductor. As pressure is increased, the resistance is reduced proportionally at all temperatures, which indicates that the scattering mechanisms do not evolve with pressure. At low temperatures (see inset), a peak develops which signals a ferromagnetic transition. Qualitatively similar behavior was seen with other samples with lower x, with the resistivity peak developing at a lower temperature. Earlier experiments verified that this peak correlates directly with the Curie temperature T_C as determined by magnetization data.[1] As pressure is increased, this peak smoothly shifts from 14 to 8.5 K at 1.5 GPa, corresponding to a 40% decrease in T_C. Upon releasing the pressure, the original properties are obtained indicating reversibility.

Magnetoresistance (MR) data also illustrate a weakening of the ferromagnetism with pressure. Figure 2(a) displays the

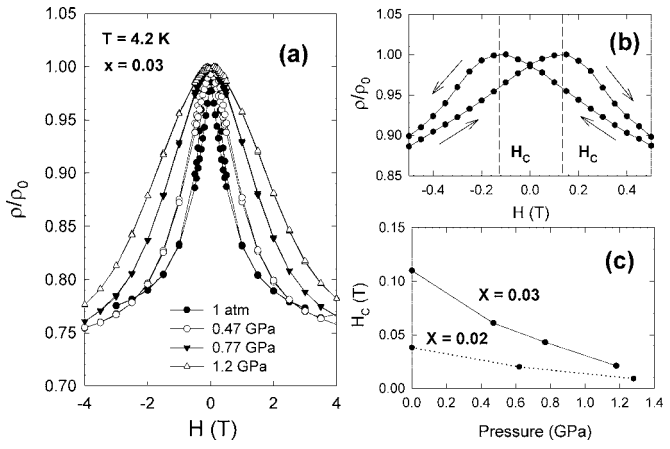

FIG. 2. (a) Pressure dependence of normalized magnetoresistance vs magnetic field at 4.2 K for $Sb_{1.97}V_{0.03}Te_3$ single crystal. (b) Atmospheric pressure magnetoresistance hysteresis loop; coercive field H_C is indicated by dashed lines. (c) Pressure dependence of the coercive field at 4.2 K.

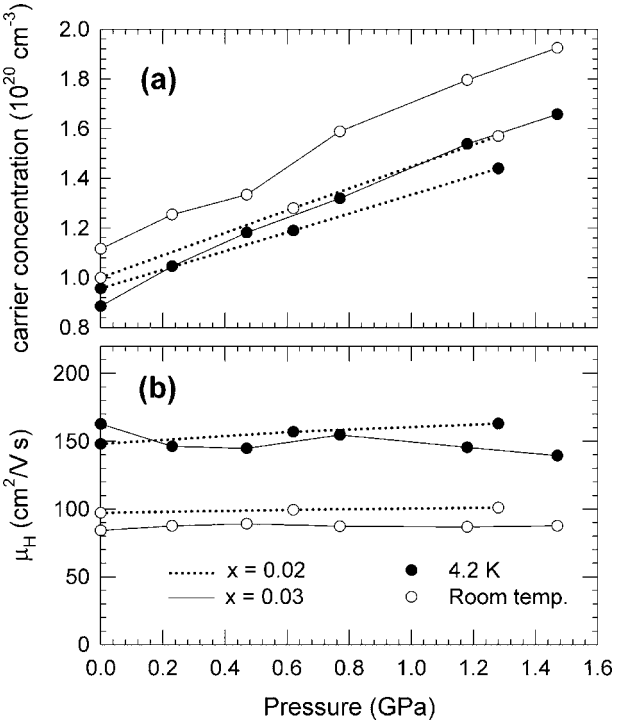

FIG. 3. (a) Free hole concentration and (b) Hall mobility at 4.2 K and room temperature as a function of pressure for $Sb_{2-x}V_xTe_3$ single crystals.

resistivity normalized to the zero field value at 4.2 K for a range of pressures in $Sb_{1.97}V_{0.03}Te_3$. Other samples showed the same behavior. Applied field causes a reduction of the spin disorder scattering resulting in a negative MR, which is directly related to the sample magnetism. Increased pressure moves T_C to lower temperatures, and hence the negative MR is less prominent. The coercive field H_C was determined from the hysteresis in MR at low fields as displayed in Fig. 2(b). Lower vanadium concentration yields a lower H_C, and Fig. 2(c) shows that pressure significantly reduces H_C for all values of x.

Hall effect measurements were carried out to uncover the dual role that carrier concentration plays in affecting both the resistivity and Curie temperature. Because the Hall coefficient is independent of magnetic field, a single band model with only one type of hole, rather than two, is favored here. This enables a straightforward determination of hole concentration from $p=1/(eR_H)$, where R_H is the Hall coefficient. The influence of pressure on the carrier concentration in $Sb_{2-x}V_xTe_3$ is illustrated in Fig. 3(a). Our data show a clear increasing trend in p with applied pressure for all samples. Further, the Hall mobility $\mu_H=R_o/\rho$ is very insensitive to pressure [see Fig. 3(b)]. By comparing to the pressure dependence of the electrical resistivity in Fig. 1 and noting that $\rho=1/pe\mu$, one can clearly see that the reduction in ρ is caused by an increase in p. The fact that mobility is roughly constant with pressure also suggests that the hole effective mass is not changing, further supporting a single band picture.

It is clear that pressure is suppressing the Curie temperature in $Sb_{2-x}V_xTe_3$ single crystals with $x \leqslant 0.03$, and we postulate that the primary cause is an increase in the hole concentration. A mean-field model is often invoked to describe T_C of DMS and predicts that $T_C \propto S(S+1)mn_ip^{1/3}$, where S is the vanadium spin $(S=1)$, m is the hole effective mass, and n_i

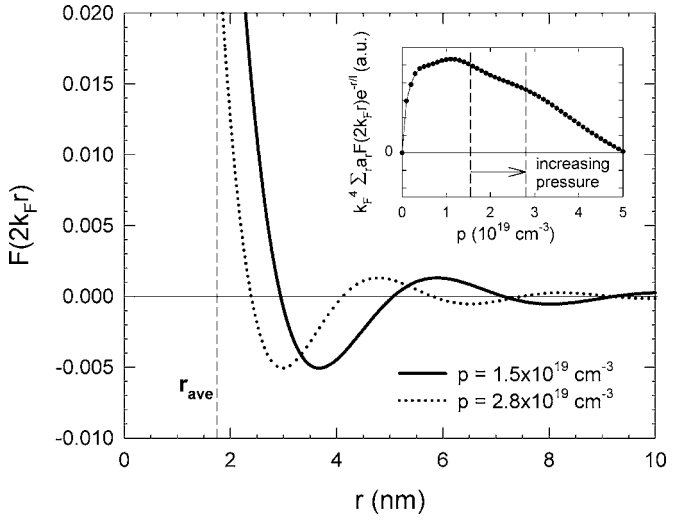

FIG. 4. Dependence of RKKY oscillatory function $F(2k_F r)$ as a function ion–ion separation r for two values of the carrier concentration. The dashed line represents the average separation between vanadium ions for $x=0.03$. (Inset) Sign of the magnetic interaction (ferromagnetic is positive) as a function of carrier concentration. The impact of pressure on carrier concentration leads to a suppression of ferromagnetism within this model.

is the concentration of magnetic ion impurities.[14,15] Our transport results above suggest a single band model with p increasing by roughly a factor of 2 at the highest pressures, while m stays constant, implying that T_C should increase. However, this model is not valid unless $p/n_i \ll 1$ (Refs. 16 and 17) and carrier mobility is small ensuring that the sign of the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction is only ferromagnetic because the first zero in the oscillating RKKY term (see below) occurs at a distance much longer than the mean free path.[18] Adopting a model of a sixfold degenerate valence band (i.e., total hole concentration divided among six equivalent carrier pockets), p/n_i increases from ~ 0.1 to ~ 0.2 with increasing pressure. In this case RKKY oscillations could lead to frustrated indirect coupling between local moments and to a suppression of ferromagnetism with increased p.

The RKKY exchange Hamiltonian between the vanadium spins at sites i and j is expressed by $H=\Sigma_{i,j} J(r_{ij})\mathbf{S}_i \cdot \mathbf{S}_j$, with $J(r) \propto m J_0^2 k_F^4 F(2k_F r) e^{-r/\ell}$. Here, r_{ij} is the distance between i and j, ℓ is the mean free path of carriers, J_0 is the local Zener coupling between vanadium local moments and hole spins, $k_F=(3\pi^2 p)^{1/3}$ is the Fermi wave number in a parabolic band approximation, and $F(x)=x^{-4}[\sin(x)-x\cos(x)]$. In Fig. 4, we plot $F(2k_F r_{ij})$ for a single carrier pocket versus r_{ij} for p of 1.5×10^{19} and 2.8×10^{20} cm^{-3}, representing the range of hole concentrations accessed by tuning pressure. The average separation between vanadium spins $r_{\mathrm{av}}=(n_i)^{-1/3}$ for $x=0.03$ is shown with a dashed line, illustrating that the first zero in F approaches r_{av} as p increases. Further, we note that mean free paths calculated from the carrier mobilities at 4 K had values of 8 ± 1 nm, encompassing several sign changes in $J(r)$. While a full calculation of the Curie temperature is beyond the scope of this paper, we explore a simplified model. Curie temperature will be proportional to $k_F^4 \Sigma_r a_r F(2k_F r) e^{-r/\ell}$, where a_r is the number of rth nearest vanadium ion neighbors. A calculation based on vanadium ion concentration distributed uniformly over a simple cubic lattice including terms out to $r_{ij} > 12$ nm is shown in the inset of Fig. 4. The sum is positive at a hole concentration per carrier pocket of 1.5×10^{19} cm^{-3}, indicating that ferromagnetism is predicted, and increase to 2.8×10^{19} cm^{-3} results in a roughly 30% decrease—a notable agreement with our reduction in T_C observed experimentally. The pressure dependence of J_0 is taken to be constant here but is expected to increase modestly as has been seen in $In_{1-x}Mn_xSb$.[9] More detailed calculations are warranted for this system, as was recently done for $Ga_{1-x}Mn_xAs$ taking into account the discrete nature of the underlying lattice and disorder in the ion distribution.[16] We note that our data are in qualitative agreement with this work, which predicts that ferromagnetism is suppressed for p/n_i in the range 0.1–0.25.

In conclusion, we have measured the transport properties as a function of magnetic field and pressure on $Sb_{2-x}V_xTe_3$ single crystals over a range of ion concentration $x=0.02-0.03$. Electrical resistivity and Curie temperature decrease significantly with applied pressure. Our Hall data indicate that the reduction in ρ is due to an increase in free hole concentration, and effective mass and scattering mechanisms are unaffected. Further, transport data are consistent with a single valence band picture, greatly simplifying comparisons to free-carrier-mediated models of ferromagnetism. Our data strongly suggest that the ferromagnetic order in this material is hole mediated and that a full RKKY theory which includes the oscillatory nature of the indirect ion–ion interaction is needed in order to explain the data.

We wish to acknowledge financial support from Research Corporation Award CC6035 (J.S.D.) and Ministry of Education Youth and sports of Czech Republic under the project MSM 0021627501 (C.D. and P.L.).

[1] J. S. Dyck, P. Hajek, P. Lostak, and C. Uher, Phys. Rev. B **65**, 115212 (2002).
[2] V. A. Kulbachinskii, A. Yu. Kaminskii, K. Kindo, Y. Narumi, K. Suga, P. Lostak, and P. Svanda, Physica B **311**, 292 (2002).
[3] J. S. Dyck, C. Drasar, P. Lostak, and C. Uher, Phys. Rev. B **71**, 115214 (2005).
[4] J. Choi, H. W. Lee, B. S. Kim, S. Choi, J. Choi, J. H. Song, and S. L. Cho, J. Appl. Phys. **97**, 10D324 (2005).
[5] T. Jungwirth, J. Sinova, J. Masek, J. Kucera, and A. H. MacDonald, Rev. Mod. Phys. **78**, 809 (2006).
[6] H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto, and Y. Iye, Appl. Phys. Lett. **69**, 363 (1996).
[7] S. U. Yuldashev, H. Im, V. S. Yalishev, C. S. Park, T. W. Kang, S. Lee, Y. Sasaki, X. Liu, and J. K. Furdyna, Appl. Phys. Lett. **82**, 1206 (2003).
[8] Z. H. Zhou, C. Uher, M. Zabcik, and P. Lostak, Appl. Phys. Lett. **88**, 192502 (2006).
[9] M. Csontos, G. Mihaly, B. Janko, T. Wojtoicz, X. Liu, and J. K. Furdyna, Nat. Mater. **4**, 447 (2005).
[10] V. A. Kulbachinskii, N. Miura, H. Nakagawa, C. Drasar, and P. Lostak, J. Phys.: Condens. Matter **11**, 5273 (1999).
[11] L. G. Khvostantsiv, A. I. Orlov, N. Kh. Abrikosov, and L. D. Ivanova, Phys. Status Solidi A **58**, 37 (1980).
[12] P. Larson, Phys. Rev. B **74**, 205113 (2006).
[13] T. Thonhouser, G. S. Jeon, G. D. Mahan, and J. O. Sofo, Phys. Rev. B **68**, 205207 (2003).
[14] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).
[15] T. Junwirth, W. A. Atkinson, B. H. Lee, and A. H. MacDonald, Phys. Rev. B **59**, 9818 (1999).
[16] D. J. Priour and S. Das Sarma, Phys. Rev. Lett. **97**, 127201 (2006).
[17] T. Dietl, A. Haury, and Y. Merle d'Aubigne, Phys. Rev. B **55**, R3347 (1997); J. Schliemann, J. Konig, and A. H. MacDonald, *ibid.* **64**, 165201 (2001).
[18] F. Matsukura, H. Ohno, A. Shen, and Y. Sugawara, Phys. Rev. B **57**, R2037 (1998).