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The structural and magnetic properties of Mn$_5$Ge$_3$C$_x$ films prepared at elevated substrate temperatures $T_S$ are investigated. In particular, films with $x \geq 0.5$ and $T_S = 680$ K exhibit a strongly enhanced Curie temperature $T_C \approx 440$ K compared to Mn$_5$Ge$_3$ with $T_C = 304$ K. Structural analysis of these films suggests that the carbon is interstitially incorporated into the voids of Mn octahedra of the hexagonal Mn$_5$Si$_3$-type structure giving rise to a lattice compression. The enhanced ferromagnetic stability in connection with the lattice compression is interpreted in terms of an Mn-Mn interaction mediated by C based on a change in the electronic structure.

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Manganese compounds exhibit a variety of properties which are of fundamental interest, such as the discovery of the colossal magnetoresistance in La$_{1-x}$Sr$_x$MnO$_3$ [1] or the quantum-critical behavior of the weak itinerant magnet MnSi [2]. Intermetallic compounds of Mn and Ge occur in several structural phases, which mostly exhibit antiferromagnetic or ferrimagnetic order with rather low ordering temperatures. However, Mn$_5$Ge$_3$ stands out as a ferromagnet with a Curie temperature $T_C = 304$ K and a uniaxial magnetic anisotropy along the $c$ axis of the hexagonal $D_{6h}$ structure (space group $P6/mmc$) [3,4]. The magnetic structure of this compound as studied by neutron scattering [3] reveals two Mn sublattices with different magnetic moments resulting in an average order magnetic moment of 2.6 $\mu_B$/Mn-atom [5].

In contrast, the isostructural Mn$_5$Si$_3$ compound is antiferromagnetic with two different magnetic phases below Néel temperatures $T_N = 68$ K and $98$ K. Consequently, a transition from antiferromagnetic to ferromagnetic behavior was found in Mn$_5$(Ge$_1-y$Si$_y$)$_3$ alloys in dependence of $y$ [6,7]. More remarkably, the antiferromagnetic Mn$_5$Si$_3$ was reported to exhibit ferromagnetic order when doped with carbon (Mn$_5$Si$_3$C$_x$), saturating at a doping-level $x = 0.22$ with $T_C = 152$ K [8]. The interstitial incorporation of carbon into the voids of Mn octahedra expands the lattice slightly and the Curie temperature $T_C$ varies almost linearly with doping level $x$. Even more interestingly, $T_C$ could be enhanced up to 350 K by incorporating carbon by simultaneous evaporation of Mn and SiC [8,11]. A shift from antiferromagnet to ferromagnet and an ensuing $T_C$ increase might be simply due to a lattice expansion as suggested by the famous Bethe-Slater curve [12]. Indeed, the monotonic $T_C(y)$ dependence in Mn$_5$(Ge$_{1-y}$Si$_y$)$_3$ [4] can be interpreted in this way. On the other hand, the incorporation of carbon might change the electronic band-structure and thus the Mn-Mn exchange. Hence, because the role of interstitial carbon in influencing the magnetic properties and stabilizing the ferromagnetic order in Mn$_5$Si$_3$ is presently not clear, it is important for an understanding to investigate the effect of C doping on the isostuctural hexagonal ferromagnetic compound Mn$_5$Ge$_3$.

In this letter we report on the magnetic and structural properties of Mn$_5$Ge$_3$C$_x$ films with a strongly enhanced Curie temperature $T_C \approx 440$ K for $x \geq 0.5$ compared to $T_C = 304$ K for undoped Mn$_5$Ge$_3$. This is even higher than $T_C = 330$ K of Mn$_5$GeC with the cubic perovskite structure [9]. Surprisingly, we find that the increase of $T_C$ upon C doping is accompanied by a decrease in the lattice constants thus demonstrating the decisive role of carbon in altering the electronic properties.

100-nm thick Mn$_5$Ge$_3$C$_x$ films were prepared by simultaneous dc- and rf-magnetron sputtering from elemental Mn, Ge, and C targets (purity 99.9%) in Ar atmosphere onto (1120) sapphire substrates at different substrate temperatures $T_S$. They were structurally characterized by x-ray diffraction in a standard powder diffractometer with Cu-$K_{α}$ radiation. Magnetic hysteresis loops were measured by the magneto-optical Kerr effect in transverse geometry ($t$-MOKE), i.e. with the magnetic field aligned in the film plane and perpendicular to the plane of incidence, for temperatures $T = 2 - 500$ K. Additionally, the saturation magnetic moment was obtained by SQUID magnetometry at $T = 5$ K with the magnetic field oriented in the film plane.

Fig. 1 shows a $θ/2θ$ x-ray diffractogram of an Mn$_5$Ge$_3$C$_{0.75}$ film prepared at $T_S = 680$ K. The observed diffraction lines can be indexed assuming the hexagonal Mn$_5$Si$_3$-type structure, apart from the strong substrate reflections and weak reflections due to precipitations of Mn$_5$Ge$_2$ (not ferromagnetic) and elemental Ge. The structure of such ternary $T_5M_3C_2$ compounds, where $T$ is a transition metal and $M$ a metalloid, has been studied in great detail [4,13]. The atomic positions in the Mn$_5$Si$_3$-type structure are 4 MnI in 4(d), 6 MnII in 6(g1), and 6 Si in 6(g2). The carbon is likely to be accommodated in voids surrounded by distorted MnI octahedra at positions 2(b) without a change of the structure while a certain percentage of the MnI 4(d) positions remain unoccupied [15]. Such phases with filled $D_{6h}$ structure (Nowotny phases) are generally non-stoichiometric due to the variable occupancy of the voids. X-ray diffractograms of samples
prepared at lower and higher $T_S$ show the formation of a strongly disordered material or precepitation of some German alloys, respectively. The observed intensities (Fig. 1) differ from the theoretically expected values indicating a strong columnar texture along the growth direction, i.e. the hexagonal $c$-axis, already reported for sputtered Mn$_5$Ge$_3$ films [1]. The texture is also inferred from the small half-width $\Delta \omega \approx 1.2^\circ$ of the $(0002)$ rocking curve (Fig. 1 inset). We mention that the powder diffraction pattern of Mn$_5$Si$_3$C$_x$ films prepared under the same conditions and detached from the substrate can be perfectly fitted by the Nowotny phase [15]. It is therefore very likely that this phase is also formed in Mn$_5$Ge$_3$C$_x$ films.

The lattice parameters determined from the diffraction lines indicate a lattice compression caused by the incorporation of C. For $x = 0.75$ we find $c = 4.996$, $a = 7.135$ and $c/a = 0.700$, i.e. a compression in each direction compared to $c = 5.053$, $a = 7.184$, $c/a = 0.703$ for Mn$_5$Ge$_3$ [3]. This is in strong contrast to Mn$_5$Si$_3$C$_x$ annealed powder samples ($x \ll 1$), where the $c/a$ ratio increases slightly and $a$ remains almost constant upon interstitial insertion of carbon [15].

Carbon doping induces a strong enhancement of the Curie temperature, reaching $T_C \approx 440$ K, i.e. well above room temperature. Fig. 3 shows the magnetization $M(T)$ for an Mn$_5$Ge$_3$C$_1.5$ film ($T_S = 680$ K) measured by $t$-MOKE, together with a hysteresis loop taken at room temperature. The distinct deviation from a square loop suggests that the easy axis of magnetization is pointing out of the film plane, i.e. along the hexagonal $c$-axis, due to the columnar texture, since the $t$-MOKE measures the in-plane component of the magnetization.

![FIG. 1. $\theta/2\theta$ x-ray diffraction pattern of an Mn$_5$Ge$_3$C$_{0.75}$ film sputtered at $T_S = 680$ K onto (1120) sapphire ($Cu$ $K_\alpha$ radiation). Miller indices refer to the hexagonal $D_{6h}$ structure, see text. Reflections due to elemental Ge, Mn$_5$Ge$_2$, and the substrate are labeled A, B, and S, respectively. Inset shows the rocking curve ($\omega$-scan) of the (0002) Bragg reflection.](image)

![FIG. 2. Temperature dependence of the magnetization $M$ in an applied magnetic field $\mu_0 H = 300$ mT measured by $t$-MOKE for a Mn$_5$Ge$_3$C$_{1.5}$ film sputtered at $T_S = 680$ K. Inset shows a hysteresis loop $M(H)$ at room temperature.](image)
microscopic investigations.

For larger concentrations $x > 0.75$ the average Mn moment decreases whereas $T_C$ remains constant. This behavior is attributed to the increased formation of non-magnetic phases which reduce the amount of the ferromagnetic phase and therefore the average moment, whereas the Curie temperature of the majority phase is still maintained. This is corroborated by an overall decrease of the magnetic signal in $t$-MOKE with increasing $x$. Furthermore, the half-width of the (0002) rocking curve increases with increasing $x$, most likely due to the decreasing columnarity of the multiphase material.

The question arises how the ferromagnetic exchange interaction can be enhanced by the incorporation of carbon. Obviously, only the Mn$_{II}$ atoms of the octahedra around the C site are affected via $sp$-$d$ interaction or hybridization. This can also be inferred from neutron scattering data on Mn$_5$(Ge$_{1-x}$Si$_x$)$_3$ [9]. The Mn$_{II}$ atoms with a moment of $\approx 3\mu_B$ seem to be strongly ferromagnetically coupled to each other while the coupling between the Mn$_I$ atoms with $\mu \approx 2\mu_B$ is certainly weaker. Substitution of Si for Ge gives rise to a reduction of the moment at the Mn$_{II}$ site whereas the Mn$_{II}$ moments remain unaffected.

In C-doped Mn$_5$Ge$_3$ two alternative possibilities may lead to the strongly enhanced Curie temperature, involving either a predominantly covalent bonding between Mn and C or an ionic charge transfer. The carbon and the surrounding Mn$_{II}$ atoms are possibly covalently bonded by $sp$-$d$ hybrid orbitals and the local environment of the nearest Mn$_{II}$ neighbors around C is comparable to the cubic Mn$_5$/M perovskites, where C is incorporated in octahedral interstices of the face-centered cubic $Mn$/M atom array [13]. In the perovskites the band structure is modified by the electronegative interstices so that the broad bands arising from the Mn-$M$ bonding are split by the changed translational symmetry and the occupation of the $sp$ states overlapping with the $d$ bands is changed by Mn-C and $M$-$C$ interactions. This may stabilize a spontaneous magnetization although the spin configuration can be complex giving rise to a ferromagnetic-to-antiferromagnetic transition at low temperatures [3]. For the present samples such band-structure effects are further complicated by the variable filling of the (4$d$) Mn$_{II}$ positions of the Nowotny phase. However, the general mechanism of changing the band-structure due to the introduction of C serving as an electron acceptor might be similar to Mn$_3$/M/C.

On the other hand, in a simple ionic picture applied to undoped Mn$_5$Ge$_3$, charge balance requires 6 Ge$^{4+}$, 4 Mn$_{II}^{3+}$, and 6 Mn$_{II}^{2+}$. The Mn$_{II}$ valence is also compatible with the magnetization density measured by neutron diffraction [9]. The addition of C will induce a charge transfer from Mn$_{II}$ atoms to C, assuming that C is strongly electronegative. This would, for instance, lead to a C$^{-4}$ ion surrounded by 4 Mn$_{II}^{3+}$ and 2 Mn$_{II}^{2+}$ ions at the corners of the octahedron, thus offering the possi-

![Figure 3](image_url)

**FIG. 3.** (a) Curie temperature $T_C$ vs. substrate temperature $T_S$ for sputtered Mn$_5$Ge$_3$C$_{1.5}$ films. (b) $T_C$ and average saturation moment $\mu_S$ in units of $\mu_B$/Mn-atom for Mn$_5$Ge$_3$C$_x$ films sputtered at $T_S = 680$ K vs. carbon concentration $x$. Solid lines serve as guides to the eye.

From neutron-diffraction data, Forsyth and Brown presented evidence that in several Mn-metalloid binary intermetallic compounds the moment reduction at different Mn-sites with respect to the free-ion value is governed by the nearest-neighbor Mn-Mn interaction. Below a critical average Mn-Mn bond length of about 3.1 Å, each Mn neighbor reduces the moment of the coordinated Mn atom from the ionic value by about $2\mu_B$/Å [9]. Applying this empirical relationship to the present samples, a magnetic moment of about 2.3 $\mu_B$ is expected from the measured lattice parameters. The additional reduction observed in the present samples can have two reasons. First, it could be due to some non-magnetic minority phases. However, this would require a high volume fraction of 50% of non-magnetic material at optimal doping $x \approx 0.75$ which seems unlikely in view of the weak parasitic x-ray Bragg reflections that could be attributed to Mn$_5$Ge$_2$ or elemental Ge. Second, if the carbon participates in the Mn-Mn bonding the simple relationship between average Mn-Mn bond length and magnetic moment will break down, because the $d$-band population and therefore $\mu_S$ is modified by the incorporation of carbon into the magnetic host lattice. Such an effect of carbon doping on the band structure has been suggested for the cubic perovskites Mn$_3$/M/C where $M$ is a non-transition metal [9]. Clearly, the magnetic moment at the different Mn sites has to be determined by further
bility of double exchange leading to ferromagnetic order as originally proposed by Zener and investigated in detail in the colossal magnetoresistance alloys. For ferromagnetic alloys of Mn or Fe the effect of interstitial non-magnetic atoms like B, C, and N, on the magnetic properties has been recently studied theoretically by assuming a Hubbard-split band at half filling coupled with a localized spin system via exchange coupling. The coupling gives rise to the double-exchange mechanism in the limit of completely localized orbitals. Whether this model or other more realistic double-exchange models including lattice distortions can be applied to the C-doped Mn$_5$Ge$_3$ alloys requires a detailed knowledge of the valences at the different Mn sites. In case of a complete charge transfer we would expect a change of the average valence from 2.4 for Mn$_5$Ge$_3$ to 3 for Mn$_5$Ge$_3$Co$_{0.75}$. We have checked this possibility by performing preliminary x-ray absorption measurements for $x = 0$ and $x = 0.75$. The experiments were done at the beamline A1 at HASYLAB, Hamburg. The absorption edge shifts to higher energies in the C-doped sample by less than 0.5 eV which corresponds to an average valence change of less than 0.1, clearly much less than the ionic model would predict. We conclude that the double exchange mechanism plays only a minor role in enhancing the ferromagnetism in Mn$_5$Ge$_3$C$_x$.

Although the facts that (i) $dT_C/dp > 0$ for pure Mn$_5$Ge$_3$ and (ii) $T_C$ increases while the volume decreases upon C doping appear to be superficially compatible, it is clear from the above discussion that the enhanced Curie temperature of Mn$_5$Ge$_3$C$_x$ is not due to a simple volume effect. This is supported by the monotonous $T_C(y)$ dependence in Mn$_5$(Ge$_{1-y}$Si$_y$)$_3$ as soon as the antiferromagnetic Mn$_2$Si$_3$ changes to ferromagnetism with increasing Ge concentration. We also note that taking $dT_C/dp = 5.5$ K/GPa for Mn$_5$Ge$_3$ and assuming a bulk modulus of $K = 110$ GPa would lead to $dT_C/d(ΔV/V) = −605$ K which is incompatible with $dT_C/d(ΔV/V) = −1700$ K derived by simply relating the volume change upon C doping to the $T_C$ change. This strongly confirms our above assignment of a predominantly electronic effect.

In conclusion, carbon doping of Mn$_5$Ge$_3$ compounds leads compression of the crystalline lattice and to a strongly enhanced ferromagnetic stability in remarkable contrast to Mn$_5$(Ge$_{1-y}$Si$_y$)$_3$ compounds, where $T_C$ decreases with decreasing lattice parameters. We have presented evidence that this is due to an increased interaction between Mm atoms mediated by interstitially incorporated carbon. The enhanced Curie temperature is attributed to a change in the electronic band structure. Our results have opened the route to a number of important investigations for the future. First of all, neutron studies are required to determine the magnetic moments at the different Mn sites. Electron-loss spectroscopy can determine the valence of carbon. Finally, the C bonding in these Mn compounds should be investigated theoretically.

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[1] R. von Helmholdt, J. Wecker, B. Holzapfel, L Schulz, and K. Sauver, Phys. Rev. Lett. 71, 2331 (1993)
[2] C. Pfleiderer, G.J.C. McMullan, S.R. Julian, and G.G. Lonzarich, Phys. Rev. B 55, 8330 (1997)
[3] L. Castellon, Monatsh. Chem. 84, 765 (1953)
[4] K. Kanematsu, J. Phys. Soc. Japan 17, 85 (1962)
[5] R. Ciszewski, phys. stat. sol. 3, 1999 (1963)
[6] J.B. Forsyth and P.J. Brown, J. Phys. Cond. Mat. 2, 2713 (1990)
[7] G. Kappel, G. Fischer, and A. Jaelge, Phys. Lett. 45 A, 267 (1973)
[8] G. Kappel, G. Fischer, and A. Jaelge, Phys. stat. sol. (a) 34, 691 (1976)
[9] P. Panissod, A. Qachau, G. Kappel, J. Phys. C 17, 5799 (1984)
[10] J.P. Sénateur, J.P. Bouchaud, and R. Fruchart, Bull. Soc. fr. Minéral. Cristallogr. 90, 537 (1967)
[11] M. Gajdzik, C. Stürgers, M. Kelemen, B. Hillebrands, and H. v. Löhneysen, Appl. Phys. Lett. 68, 3189 (1996)
[12] See, e.g., B.D. Cullity, Introduction to Magnetic Materials, (Addison-Wesley, Reading, 1972)
[13] J.B. Goodenough and J.M. Longo in: Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, New Series, Vol. 4a, K. H. Hellwege (Ed.), (Springer, Berlin, 1970) pp. 263 and references therein
[14] W. Jeitschko, H. Nowotny, and F. Benesovsky, Monatsh. Chem. 94, 844 (1954)
[15] E. Parthé, W. Jeitschko, and V. Sadagopan, Acta. Cryst. 19, 1031 (1965) and references therein
[16] E. Sawatzky, J. Appl. Phys. 42, 1706 (1971)
[17] M. Gajdzik, C. Stürgers, and H. v. Löhneysen, to be published
[18] C. Zener, Phys. Rev. 82, 403 (1951)
[19] For a recent review see, e.g., A.P. Ramirez, J. Phys.: Cond. Mat. 9, 8171 (1997)
[20] A. Sakuma, J. Magn. Magn. Mater. 173, 173 (1997)
[21] M.Y. Apte and C. Mande, J. Phys. C 15, 607 (1982)
[22] A.A. Sevast扬ov, S.M. Barmin, S.Y. Kortov, R.P. Kreentsis, and P.V. Geld, Sov. Phys. Solid State 25, 2078 (1983)
[23] H. Ido, T. Suzuki, T. Kaneko, J. Phys. Soc. Japan 29, 1490 (1970)
[24] The bulk modulus was estimated from the elastic moduli of Mn$_5$Si$_2$, Z.A. Istomina, G. P. Zinoveva, L.P. Andreeva, P.V. Geld, and A. Mikhelson, Fiz. Tverd. Tela 22, 281 (1980), by using the Voigt approximation.