Thermal expansion of monogermanides of 3d-metals

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Abstract
Temperature dependent powder and single-crystal synchrotron diffraction, specific heat, magnetic susceptibility and small-angle neutron scattering experiments have revealed an anomalous response of MnGe. The anomaly becomes smeared out with decreasing Mn content in Mn$_{1-x}$Co$_x$Ge and Mn$_{1-x}$Fe$_x$Ge solid solutions. Mn spin state instability is discussed as a possible candidate for the observed effects.

Keywords: MnGe, B$_2$0 structure, Debye–Gruneisen model, interatomic distances

(Some figures may appear in colour only in the online journal)

1. Introduction

The monosilicides and monogermanides of Mn, Fe, Co with a B$_2$0 crystal structure are composed of close elements in the periodic table but exhibit surprisingly various magnetic and electronic properties [1–3]. Moreover, their properties depend remarkably on temperature, pressure and applied strain [4–6]. MnSi, FeGe, MnGe are helimagnetic below some temperature and demonstrate metallic properties at ambient conditions, while under pressure MnGe is reported to become half-metallic [2, 7]. FeSi is a paramagnet and a small bandgap insulator, which undergoes a transition to a metal state on heating [8–10]. CoSi and CoGe have very small averaged magnetic moment per formula unit. They are metals but with a low carrier density [11].

The B$_2$0 phase has space group P2$_1$3, which is cubic but of rather low symmetry (figure 1(a)). Two atoms in the asymmetric part of the unit cell occupy the 4a (u, u, u) positions, e.g. the atom position parameters u for MnSi are $u_{\text{Mn}} = 0.138$ and $u_{\text{Si}} = 0.845$ [12]. In the so-called ideal B$_2$0 structure the atoms would be placed at $u_{\text{ideal}} = (1/4\tau) \approx 0.154 5085$ ($\tau = (1 + \sqrt{5})/2$ is the golden mean) [13, 14]. The nearest neighbor coordination of each atom would be seven equidistant atoms of the opposite kind. These seven atomic sites lie on seven of the twenty vertices of a pentagonal dodecahedron centered on the atom. Interestingly, none of the abovementioned monosilicides and monogermanides has the ideal B$_2$0 structure, the atoms are slightly shifted from their ideal positions. It results in splitting of the 7 bonds into one short, three of medium length, and three long ones, we denote the respective interatomic distances as $d_1$, $d_2$ and $d_3$ [15, 16] (figure 1(b)). Though the difference in the interatomic distances is small, the distortion of the B$_2$0 structure from its ideal form has an essential effect on the physical properties.

Of particular interest are the B$_2$0 compounds with helimagnetic properties, where complex chiral magnetic objects—spirals and skyrmions—inherit chirality from the crystal
structure via the Dzyaloshinski–Moriya interaction [17–24]. MnSi may serve as the most intensively studied example. Coupling of crystal structure with magnetism is likely to be the reason for MnSi to have the anomaly of the thermal expansion coefficient, firstly observed in [25]. The authors of [26] showed that the coefficient of thermal expansion exhibits a sharp drop at the magnetic ordering temperature along with a shoulder on the high-temperature side. An extensive study of MnSi thermal properties [17, 27, 28] uncovered a similar shoulder for heat capacity on the high-temperature side of the corresponding peak at the phase transition; such pre-transition behaviour was tentatively linked to spin fluctuations.

MnGe, a compound isostructural to MnSi with a bigger unit cell dimension, shows an even more complex magnetic response. Particularly, the helix pitch for MnGe is considerably shorter. In spite of larger Mn–Mn separation, both the magnetic ordered moment per Mn atom and the magnetic ordering temperature are higher for MnGe (the respective magnetic moments for MnGe and MnSi $\approx 2 \mu_B$ and $\approx 0.4 \mu_B$; $T_c^{\text{MnGe}} \approx 130 \text{ K}$ and $T_c^{\text{MnSi}} \approx 29 \text{ K}$) [29–31]. Small angle neutron scattering revealed an intricate ordering scenario comprising a new intermediate phase between 150 and 300 K not met for MnSi [29]. The scattering data agree with inhomogeneous character of this phase that can be seen as a mixture of ferromagnetic droplets embedded in a paramagnetic matrix.

Recently, the inhomogeneous nature of this intermediate phase in MnGe was approached with muon spin rotation, x-ray emission spectroscopy and other techniques [32, 33]. It was proposed that short-range and long-range spin fluctuations coexist in a broad temperature range. Short-range ferromagnetic inhomogeneities were reported to persist up to at least 250 K, which is fairly above 150 K corresponding collapse of long helimagnetic order. The authors of [32] assumed that the inhomogeneity of this intermediate phase is associated with the presence of both high spin and low Mn spin states. Besides, spin transition from high spin to low spin state was recently proposed for MnGe to occur under pressure [2, 7].

Here we report the results of synchrotron powder and single crystal diffraction experiments as functions of temperature for MnGe and for solid solutions Mn$_{1-x}$Co$_x$Ge and Mn$_{1-x}$Fe$_x$Ge. The data on unit cell thermal expansion, atom position parameters and interatomic distances as a function of temperature are complemented with heat capacity, magnetization and small angle neutron scattering experiments. The derived results serve as a discriminative input for the discussion of microscopic reasons for non-conventional magnetic behavior of MnGe. Particularly, the magnetic peculiarities of MnGe is linked to the distortion of the B20 structure from its ideal form, which increases upon heating. The thermal expansion is strongly enhanced, it is mostly accounted for by the extension of the nearest-neighbor Mn–Ge interatomic distances $d_3$.

The paper is organized as follows. Section 2 describes the production of the powder and single-crystal samples. It also provides some details on the performed experiments and data processing. Section 3 considers the respective results of the magnetic measurements by AC susceptibility and small-angle neutron scattering (SANS); thermal expansion by x-ray powder diffraction, heat capacity by thermal relaxation calorimetry, atomic arrangement by single-crystal x-ray diffraction. In section 4 the obtained results are discussed. The brief conclusions and acknowledgements are presented in sections 5 and acknowledgements, respectively.

2. Experiment

The polycrystalline samples were synthesized under high pressure of 8 GPa by melting the constituent elements mixed in a stoichiometric ratio with an electric current. After that the samples were rapidly quenched to the room temperature where the pressure was released (see [34] for details).

Single-crystal MnGe sample was produced by means of high-pressure high-temperature synthesis using a 1200-tonne multi-anvil press at the Bayerisches Geoinstitut (BGI, University of Bayreuth, Germany). The crystal size was $\sim 10 \mu m$. 

Figure 1. (a) The unit cell of the cubic $B20$ crystal structure of MnGe. The unit cell consists of four manganese and four germanium atoms. (b) Coordination polyhedron of Ge. The longest Mn–Ge distance is $d_3$. 

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curves following [42, 43], see and integrated for MnGe and the lattice parameter the Rietveld refinement was done for with Fit2D [38]. In order to obtain temperature variation of the powder diffraction patterns were azimuthally integrated K temperature step for a better temperature sampling. All The MnGe sample was measured additionally with the 1

...temperatures related to the maxima of... (b) The characteristic temperatures related to the maxima of d(χT)/dT and integrated SANS intensity.

For more details of the synthesis we refer to [35] and references therein.

AC susceptibility measurements were made with a SR830 lock-in amplifier in a large compensated coil system (see [36] for more details).

Small-angle neutron scattering experiments were carried out at SANS-1 at FRM-II (Munich, Germany). Neutrons with a mean wavelength of 0.6 nm were used. The sample-detector distance was set to 2.2 m. The scattering intensity was measured in zero-field cooling mode from 300 to 5 K.

Powder diffraction data were collected using Pilatus@ SNBL diffractometer (Swiss Norwegian Beam Lines at ESRF, Grenoble, France) [37]. The beam size was set to 0.25 mm, a Pilatus 2M pixel area detector was used for data recording. Geometrical parameters of the diffractometer and the wavelength 0.6888 Å were calibrated with the LaB₆ NIST 660a standard. A sample was crushed into a fine powder and placed into 0.1 mm capillary. The temperature, controlled by Cryostream 700, was varied in the 80–500 K range, with the 170–240 K h⁻¹ rate and the 2.5 K step. The MnGe sample was measured additionally with the 1 K temperature step for a better temperature sampling. All the powder diffraction patterns were azimuthally integrated with Fit2D [38]. In order to obtain temperature variation of the lattice parameter the Rietveld refinement was done for every temperature (sequential refinement) with the Fullprof software package [39].

The same experimental setup was used for single-crystal diffraction of the MnGe crystal. The data were collected at the temperatures from 80 to 290 K with the 5 K step. The wavelength of the synchrotron radiation was set to 0.68239 Å. The data were recorded with single phi-scan and 0.1° slicing. The single-crystal data were preprocessed with SNBL Tool Box [37], the integral intensities were extracted from frames with CrysAlisPro software [40], the crystal structure was solved with SHELXS and refined with SHELXL [41].

Heat capacity measurements for MnGe were performed in a PPMS-9 (Quantum Design) at St. Petersburg State University. The PPMS-9 was utilized as a thermal-relaxation calorimeter. A micro-heater and thermometer were attached to the bottom side of the sample platform. The sample was mounted to the platform by using a thin layer of grease, which provided the required thermal contact to the platform. The vacuum greases Apiezon N and Apiezon H were used in the temperature ranges of 80–300 K and 200–400 K respectively. The grease heat capacity was considered as an instrumental function. The heat capacities of the sample measured with Apiezon N and Apiezon H in the range of 200–300 K are in a good agreement. Thorough inspection of the heat capacity was carried out by means of accurate subtraction of the grease contribution and small temperature step. In the following we will deal with molar heat capacity, which is the heat capacity related to one mole of a substance.

3. Results

3.1. Magnetic susceptibility and SANS

Figure 2(a) (upper panel) exemplifies temperature dependence of the AC magnetic susceptibility for Mn₀.₇Co₀.₃Ge as compared with MnGe (the latter was taken from [29]). Both curves exhibit somewhat broad asymmetric peaks. Similar maxima are characteristic of the other samples under study. To determine the magnetic ordering temperature we used the peaks position in d(χT)/dT curves following [42, 43], see figure 2(a) (upper panel).

Furthermore small-angle neutron scattering (SANS) enabled us to explore the magnetic behaviour (see [29] for more details). The SANS maps were integrated over the entire momentum transfer range measured by the detector. Figure 2(a) (lower panel) compares the integrated SANS intensity for MnGe and Mn₀.₇Co₀.₃Ge. The maxima positions were utilized for estimation of the magnetic ordering temperature.

Figure 2(b) summarises the data on the characteristic temperatures for all the samples under study obtained from the SANS and susceptibility measurements. It is seen that the data derived with the help of different techniques agree within experimental error. The critical temperatures as a function of cobalt concentration show fast decrease with increasing cobalt concentration and saturate at ≈20 K for x > 0.4.
3.2. Powder x-ray diffraction

The powder x-ray diffraction patterns for all the samples possess weak diffraction peaks of a few additional phases. Therefore, only the unit cell dimensions were used for evaluation of the thermal expansion. This approach enabled us to probe predominantly the phase of interest [35].

Figure 3 illustrates the temperature evolution of the unit cell dimensions for Mn$_x$Co$_{1-x}$Ge series. Note that the data were normalized to the room temperature lattice parameters in order to highlight the difference in thermal expansion.

Unit cell dimensions as a function of temperature were parametrised with the Debye–Grüneisen equation, see e.g. [35, 44]. The derived parameters are the following: $a_0$ is the unit cell dimension approximated to 0 K, $\Theta_D$ is the Debye temperature, $\alpha$ is the high temperature asymptote of thermal expansion coefficient. These parameters for Mn$_{1-x}$Fe$_x$Ge (from [35]) and for Mn$_{1-x}$Co$_x$Ge are shown in figures 4(a)–(c).

The coefficient of thermal expansion ($CTE$) as a function of temperature was calculated as

$$CTE = \frac{1}{a(T)} \frac{da(T)}{dT}$$  \hspace{1cm} (1)

and it is shown in figure 5 for MnGe and Mn$_{0.05}$Fe$_{0.95}$Ge. One remarkable feature made clear by this plot is that at temperatures lower than $\sim$200 K the $CTE$ for different materials are close, while at the temperatures above $\sim$200 K the thermal expansion coefficient for MnGe is markedly enhanced.

3.3. Heat capacity

The experimental heat capacity at constant pressure $C_p$ for MnGe is shown in figure 6. Figure 6 also presents literature data from [2] on heat capacity of CoGe, which does contain only phonon contribution. In addition, the heat capacity after electronic contribution subtraction for MnGe is given$. In the

$^8$ As shown in [2] the Sommerfeld coefficient for CoGe $\gamma$ is $\sim$0 mJ mole$^{-1}$ K$^2$ and it has negligible average magnetic moment per formula unit, which implies the absence of electronic and magnetic contributions to the heat capacity. In contrast for MnGe $\gamma$ is $\sim$16 mJ mole$^{-1}$ K$^2$, the electronic contribution was estimated as $\gamma$T.

Figure 3. The temperature evolution of the unit cell parameters for Mn$_x$Co$_{1-x}$Ge normalized to the respective room temperature values, i.e. 4.7947 Å and 4.6454 Å for MnGe and Mn$_{0.05}$Co$_{0.95}$Ge, respectively.

Figure 4. The concentration dependences obtained from the Debye–Grüneisen parametrization of thermal expansion (a) the lattice parameter $a_0$ at $T = 0$ K, (b) the Debye temperature $\Theta_D$ and (c) the high temperature asymptote of thermal expansion coefficient $\alpha$. The data are presented for Mn$_{1-x}$Fe$_x$Ge (open circles) (from [35]) and for Mn$_{1-x}$Co$_x$Ge (squares). The solid curves are guides to the eyes.

Figure 5. The temperature dependence of thermal expansion coefficient for the samples with high Mn (MnGe) and high Co (Mn$_{0.05}$Co$_{0.95}$Ge) content. The data for MnGe minus the electronic contribution is marked with an asterisk. The solid curves were obtained from simulated heat capacity data at constant volume $C_v$ in terms of the Debye model with the Debye temperature of 350 K. Herewith the simulated heat capacity curves were multiplied by some scale factors.

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following we will consider this heat capacity without electronic contribution.

No extra peak at Curie temperature is observed for MnGe, thus any first order transition can be ruled out. The heat
capacity data for MnGe systematically deviate from the measurements obtained for non-magnetic CoGe on heating, see figures 6 and 9.

3.4. Single-crystal x-ray diffraction

The synchrotron single-crystal diffraction data agree well with the previously reported results on MnGe structure, which is available only at 90 and 250 K [35]. The quality of the structure refinement is also similar, 77 unique reflections were processed with the final $R$ indices $I > 2\sigma$ varying in the following ranges, $R_I \sim 0.025-0.031$, $wR_2 \sim 0.050-0.055$. The atom position parameters $u_Mn$ and $1 - u_Ge$ for MnGe as a function of temperature are given in figure 7. It is seen that the Mn sublattice varies more than the Ge sublattice.

Figure 8 shows the relative interatomic distances (normalized to the corresponding values at 300 K). What is most striking about this figure is the variation of $d_3$. At the temperatures lower than $\sim 150$ K it changes slightly as the other distances in the whole measured temperature range. While in the range of $\sim 150-300$ K $d_3$ exhibits a noticeable growth rate.

4. Discussion

Figures 4((a) and (c)) shows that the concentration dependences of $a_0$ and $\alpha$ (derived from the Debye–Grüneisen parametrisation of the thermal expansion data) are quite linear. Surprisingly, the Debye temperatures obtained from the parametrisation vary in the broad range from 450 K for Mn$_{0.05}$Co$_{0.95}$Ge to about 750 K for MnGe (figure 4(b)). On the contrary, substitution of Mn for Fe or Co in MnSi keep Debye temperature unchanged [45]. Moreover, recent measurements of the heat capacities of MnGe, FeGe and CoGe [2] correspond to characteristic Debye temperatures much lower (of about 300 K) than those fitted from the temperature dependences of the unit cell dimension. So, the comparison of the Debye temperatures from the heat capacities and $CTE$ data suggests that the fitting of the $CTE$ with the Debye–Grüneisen model represents a certain parametrisation with some effective parameters.

According to the Grüneisen quasi-harmonic model the temperature dependence of heat capacity at constant volume and $CTE$ should show the same temperature dependence (see e.g. [46]). In order to match the heat capacity data with the $CTE$ data we multiplied the Debye heat capacity with the Debye temperature of 350 K by a certain scaling factor. A good correspondence was obtained in the case of Mn$_{0.05}$Co$_{0.95}$Ge (figure 5). The Grüneisen parameter derived from the scaling factor
is 1.9. For MnGe this approach works either above room temperature or below 150 K being in agreement with our previously reported findings on anomalous thermal expansion of MnGe [47]. The temperature evolution of CTE may be seen as a crossover between two states limited by the solid curves in figure 5. Microscopically, the considerable increase of CTE for MnGe in the range of 150–300 K manifests an essentially anisotropic behavior, i.e. the interatomic distances $d_1$ extend upon heating more rapidly than the other Mn–Ge distances. In other words, it implies that there exist soft ($d_3$) and rigid ($d_1$, $d_2$) Mn–Ge bonds. Judging from atom position parameters the crystal structure is gradually moving off from the ideal B20 structure with increasing temperature but without change of the symmetry.

Comparing the heat capacities for MnGe (without electronic contribution) with that of practically non-magnetic CoGe (inset in figure 6) one sees a negative contribution for MnGe above the ordering temperature. This anomaly progressively evolves with temperature. Notably, this incremental contribution to the heat capacity of MnGe over that of CoGe can be scaled with the corresponding CTE data (figure 9), herewith the scaling factor turned out to be negative. It resembles the negative magnetic heat capacity observed for MnSi at the temperatures higher the helimagnetic ordering temperature [28].

Thus, the intermediate phase existing in MnGe upon transition from helimagnetic to paramagnetic state according to the magnetic susceptibility and SANS data is accompanied by a thermodynamic anomaly, i.e. a significant anisotropic deformation of Mn–Ge bonding. The crossover of CTE between the two states can be associated with the presence of different spin configurations linked to different unit cell volumes and effective magnetic moments per formula unit. Indeed the magnetically inhomogeneous phase was recently considered as a fluctuating mixture of metastable low spin state and high spin state [32]. Such a scenario assumes that ferromagnetic doublets observed in [29] by neutron scattering should be associated with regions enriched with high spin states. To place our results on the unusual behavior of particular Mn–Ge distances into context, one may suggest that the spin state of transition metal has an anisotropic impact on the Mn–Ge bonds.

5. Conclusion

To conclude, we have observed and characterized an anomalous thermodynamic response to the complex magnetic ordering scenario in MnGe. The deviation of the thermal expansion and heat capacity from the quasi harmonic model persists up to high temperatures. The thermal expansion coefficient and the longest Mn–Ge distance undergo an unusual increase in the broad temperature range of 150–300 K. In the same temperature range an inhomogeneous magnetic phase has been revealed by neutron diffraction; we believe that it is not a fortunate coincidence but an illustration of a link between macroscopic properties and some kind of correlated disorder. We propose spin state instability as the most probable candidate for such a disorder. In our further studies we intend to explore the pressure evolution of the interatomic distances in MnGe.

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