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Neutron diffraction study of MnNiGa₂ - Structural and magnetic behaviour

Abstract

MnNiGa₂ crystallizes in the L21 (Heusler) structure and has a ferromagnetic ordering temperature TC ~ 192 K. Rietveld refinement of the neutron diffraction patterns indicates that the Ga atoms occupy the equivalent 8c position, while Mn and Ni share the 4a (0, 0, 0) and 4b (0.5, 0.5, 0.5) sites with a mixed occupancy of Mn and Ni atoms. It is found that that ~83% of Mn and ~17% Ni are located at the 4a site while ~83% of Ni and ~17% Mn occupy the 4b site. There is no evidence of a magneto-volume effect around TC. In agreement with this finding, our detailed critical exponent analyses of isothermal magnetization curves and the related Arrott plots confirm that the magnetic phase transition at TC is second order.

Keywords

diffraction, magnetic, structural, mnniga2, study, behaviour, neutron

Disciplines

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Neutron diffraction study of MnNiGa₂—Structural and magnetic behaviour

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MnNiGa₂ crystallizes in the L21 (Heusler) structure and has a ferromagnetic ordering temperature $T_C \sim 192$ K. Rietveld refinement of the neutron diffraction patterns indicates that the Ga atoms occupy the equivalent 8c position, while Mn and Ni share the 4a (0, 0, 0) and 4b (0.5, 0.5, 0.5) sites with a mixed occupancy of Mn and Ni atoms. It is found that that $\sim 83\%$ of Mn and $\sim 17\%$ Ni are located at the 4a site while $\sim 83\%$ of Ni and $\sim 17\%$ Mn occupy the 4b site. There is no evidence of a magneto-volume effect around T_C . In agreement with this finding, our detailed critical exponent analyses of isothermal magnetization curves and the related Arrott plots confirm that the magnetic phase transition at T_C is second order. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4857455>]

Ferromagnetic shape memory alloys are of great technical interest due to their unusual properties that provide new possibilities for applications as sensors and actuators [see, e.g., Ref. 1]. Interest in Mn-Ni-Ga-based ferromagnetic shape memory alloys continues unabated due to their unique magnetoelastic properties.^{2,3} Of particular interest is the interplay between structural and magnetic properties and their role in determining shape memory behaviour. Much of the research has centred on the alloy MnNi₂Ga, which orders ferromagnetically at $T_C \sim 368$ K and undergoes a martensitic transformation at $T_m \sim 337$ K.² Due to the brittleness of MnNi₂Ga, the search for new materials has attracted significant interest in recent years.⁴ Barman *et al.*⁴ predicted the existence of a ferromagnetic shape memory alloy MnNiGa₂ using density-functional theory and confirmed that the Ga atoms occupy the equivalent 8c sites (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) based on their x-ray data. Given that the atomic numbers of Mn (25), Ni (28), and Ga (31) are similar and that the order-dependent structure factors in the Heusler structure are small, determining the site occupancies from x-ray diffraction (XRD) becomes extremely difficult.⁵ On the other hand, because of the significant differences in nuclear coherent scattering amplitudes of Mn (-3.73 fm), Ni (10.3 fm), and Ga (7.23 fm), neutron diffraction allows better discrimination of site occupancies.

In this presentation, we report on the crystallographic and magnetic structure of MnNiGa₂.

The MnNiGa₂ sample was prepared by arc-melting method and followed by annealing at 750°C for 3 days. The quality of the sample was checked by both XRD and thermomagnetic analysis. The magnetic properties of the compound were measured

in a superconducting quantum interference device (SQUID) and a Quantum Design Physical Property Measurement System (PPMS) over the temperature range of 10–300 K for magnetic fields $B = 0$ –5 T. The powder neutron diffraction patterns were collected on the high resolution powder diffractometer SPODI of FRM II, Germany with $\lambda = 1.548$ Å (for $T = 3$ –300 K) and $\lambda = 2.536$ Å (for $T = 3$ K and 300 K).

The x-ray diffraction at room temperature confirms that the MnNiGa₂ compound crystallizes in the L21-type (Heusler) structure. DC magnetization measurements (as shown in Figure 1(a)) indicate that below ~ 200 K the compound is in the ferromagnetic state. The sample has been measured in an applied field of $H = 50$ Oe on warming after first cooling in zero field (marked as ZFC). The field-cooled cooling magnetization curve, FC, was then recorded on cooling in the same field of $H = 50$ Oe from 300 K to 5 K after ZFC. It can be seen from Figure 1(a) that different thermo-magnetic behaviours are detected for the ZFC and FC magnetization curves. This behaviour can be ascribed to the magneto-history effect originating from the narrow magnetic domain pinning.⁶ Moreover, it can be seen that below ~ 55 K there exists a clear drop of magnetization in the FC magnetisation versus temperature curve with decreasing temperature, indicating the presence of anti-parallel magnetic coupling in this compound. The value of T_C has been derived to be 192 K that is very different from the value reported ($T_C \sim 330$ K) by Barman *et al.*,⁴ which may be due to compositional differences.⁷

As is also evident from Fig. 1(a) (right scale—inverse magnetisation versus temperature), for temperatures above ~ 240 K, i.e., well above $T_C = 192$ K, the inverse susceptibility follows Curie–Weiss (C–W) behaviour. Below ~ 240 K, however, a pronounced deviation from the C–W law is

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FIG. 1. (a) Temperature dependence of the magnetization $M(T)$ (left axis) and inverse magnetization $M^{-1}(T)$ (right axis) of MnNiGa_2 and (b) magnetization as a function of temperature and field in the region of the Curie temperature $T_C = 192$ K of MnNiGa_2 .

observed, reflecting the presence of short-range FM ordering above T_C in this compound.⁸

In order to fully understand the magnetic behaviour of MnNiGa_2 around T_C , we have measured the variable temperature magnetization curves with a typical set of magnetisation versus field curves shown in Figure 1(b). The positive slopes of the Arrott-plots confirm that the magnetic transition around

T_C is of second order. According to the conventional static scaling law, the critical properties of a second-order magnetic transition can be described by the critical exponents β , γ , and δ as derived from magnetization measurements around the transition temperature. We use the Kouvel-Fisher (KF) method and the critical isotherm analysis at T_C to determine the critical exponents⁹ as drawn in Figures 2(a) and 2(b). The values of $\beta = 0.42$, $\gamma = 1.12$, and $\delta = 3.9$ have been derived. The mean field interaction model for long range ordering¹⁰ has theoretical critical exponents of $\beta = 0.5$, $\gamma = 1.0$, and $\delta = 3.0$, while theoretical values based on the three dimensional Heisenberg model corresponding to short range interactions are $\beta = 0.365$, $\gamma = 1.386$ and $\delta = 4.80$ [see, e.g., Ref. 11]. The values we have derived for β , γ and δ for MnNiGa_2 are close to the mean field model—indicating that long range ordering is dominant. According to the prediction of the scaling equation, the magnetic equation can be written as $M(H, \varepsilon) = \varepsilon^\beta f_{\pm}(H/\varepsilon^{\beta+\gamma})$, where $f_{\pm}$ are regular functions with f_{+} for $T > T_C$ and f_{-} for $T < T_C$. $\varepsilon = (T - T_C)/T_C$ is the reduced temperature. Using the values of β and γ obtained above, we plotted the graph of M/ε^β versus $H/\varepsilon^{\beta+\gamma}$ as shown in Figure 2(c), which yields two universal curves, one for temperatures above T_C and the other for temperatures below T_C , in agreement with the scaling theory.

The magnetic entropy values, $-\Delta S_M$, around ferromagnetic ordering temperature for fields up to $B = 5$ T were derived from the magnetisation measurements using the standard Maxwell relationship as shown in Fig. 2(d). The changes in maximum magnetic entropy were plotted as a function of H around T_C in the inset on $\log_{10}$ - $\log_{10}$ scale. The valid linear-relationship of $-\Delta S_M \propto (H/T_C)^{2/3}$ confirms that the magnetic phase transition around T_C belongs to second order as derived above.

As mentioned above, since the neutron scattering amplitudes of the three elements Mn, Ni, and Ga are significantly different, we carried out a detailed neutron diffraction investigation from 3 K to 300 K ($\lambda = 1.548$ Å) to determine the atomic occupancies. In addition, we collected patterns at $T = 3$ K and 300 K with longer wavelength ($\lambda = 2.536$ Å).

FIG. 2. (a) The critical isotherm analysis of MnNiGa_2 at T_C . The inset shows the plot on a $\log_{10}$ - $\log_{10}$ scale with a fitted solid line; (b) Kouvel-Fisher plot for the spontaneous magnetization $M_{so}(T)$ and the inverse initial susceptibility $\chi_o^{-1}(T)$ (solid lines are fitted); (c) scaling plots around T_C using β and γ determined by the KF method (only a few typical curves are shown); and (d) temperature dependence of the isothermal magnetic entropy change $-\Delta S_M(T, H)$. The inset shows the dependence of the entropy change $-\Delta S_M$ on the parameter $(H/T_C)^{2/3}$.

FIG. 3. (a) Rietveld refinements of neutron diffraction patterns of MnNiGa_2 at 300 K and 3 K. The variation of the magnetic R-factor (R_{mag}) with moment on the 4a site is shown in the inset (see text); (b) representative neutron diffraction patterns over of 3–300 K ($\lambda = 1.548 \text{ \AA}$); the inset shows the temperature dependence of the intensities of the (111) and (200) reflections; and (c) the variation in the lattice parameter a of MnNiGa_2 with temperature. The dashed lines in (c) represent the phonon contribution to the thermal expansion with Debye temperature $\theta_D = 300 \text{ K}$.

The low temperature pattern provided enhanced signals from the magnetic contributions while the higher temperature patterns (above T_C) were used to obtain information about the atomic occupancies. The diffraction patterns have been refined using the FULLPROF program package. The best refinements of the 300 K patterns indicate that Ga atoms occupy the (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) sites, which agrees well with the reported data based on X-ray results.⁴ However, we found that the Mn and Ni atoms share

the 4a (0, 0, 0) and 4b (0.5, 0.5, 0.5) sites with a mixed occupancy of Mn and Ni atoms. Rietveld refinements of the neutron diffraction patterns (e.g., Fig. 3(a)) indicate that $\sim 83\%$ of Mn and $\sim 17\%$ Ni are located at the 4a site while $\sim 83\%$ of Ni and $\sim 17\%$ Mn occupy the 4b site. Given that x-rays cannot readily distinguish the difference of Ni and Mn, it is not surprising that this mixed occupancy could not be detected.⁴

In principle, while magnetic diffraction can provide information about the magnetic structure of materials,¹² in the case of MnNiGa_2 , we found that the magnetic intensities are extremely low (see inset of Figure 3(b)); correspondingly free refinement of the crystal structure parameters and magnetic moments on metal sites led to unstable fits. We therefore imposed some reasonable constraints to refine the neutron patterns collected below the magnetic transition temperature: (1) we fixed the occupancy factors determined from the room temperature; (2) an overall magnetic moment was varied for each metal site rather than for individual Mn and Ni moments; (3) the total moment was fixed to the value of spontaneous magnetization from our magnetic measurements (e.g., $M_s = 0.85 \mu_B$ at 10 K). A number of refinements were then carried out with the moment on the 4a and 4b sites allowed to vary in the range from $-1.4 \mu_B$ to $2.1 \mu_B$ with a step ($\Delta = 0.2 \mu_B$). As drawn in the inset of Figure 3(a), the magnetic R-factor (R_{mag}) demonstrates two minima (mirror type): $M_{4a} = -0.65 \mu_B$ and $M_{4a} = 1.50 \mu_B$. Considering the symmetry of MnNiGa_2 (Fm-3m), we conclude that there exists linear anti-parallel coupling between moments at the 4a and 4b site and the moments are determined to be $M_{4a} = -0.65 \mu_B$ and $M_{4b} = 1.50 \mu_B$. The temperature dependence of the lattice constant as derived from the refinements is shown in Fig. 3(c) with no indication of an obvious magnetovolume effect around T_C . This is also emphasised by the dashed line through the data in Fig. 3(c), which represents the phonon contribution to the thermal expansion for Debye temperature $\theta_D = 300 \text{ K}$.¹³

Detailed investigations of the magnetic and structural behaviours of MnNiGa_2 below 300 K have shown that the Ga atoms occupy the equivalent sites 8c, while Mn and Ni show a mixed occupancy at both the 4a and 4b sites. The magnetic atoms at 4a and 4b sites show an antiparallel coupling with the moment values of $0.65 \mu_B$ and $1.50 \mu_B$, respectively, as estimated by a constrained Rietveld analysis. The magnetic phase transition at T_C is shown to be second order with detailed critical exponent analyses demonstrating that long-range order magnetic interactions dominate.

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