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High Pressure Synchrotron X-ray Diffraction study of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy

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Abstract

High pressure x-ray diffraction studies up to 10.4 GPa were performed on the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy using synchrotron radiation with a diamond anvil cell. No structural phase transitions occurred in the entire range of our measurements. Unit cell parameters were determined up to 10.4 GPa and the calculated unit cell volumes were found to be well represented by a third order Birch-Murnaghan equation of state. The bulk modulus determined from the pressure – volume data was found to be, $B_0 = 231.72 \pm 7.79$ GPa. This study, employing high resolution synchrotron x-rays has helped clarify the behaviour of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy under high pressure.

Keywords: Alloys; Magnetic property; High pressure effect; Magnetocaloric effect

1. Introduction

So far, research has tended to rely primarily on the use of chemical substitution to prepare novel magnetocaloric materials. This focus has tended to overlook in a way, the use of pressure tuning to improve the magnetocaloric properties of these materials. Normally, chemical pressure is used to simultaneously tune separate magnetic and crystallographic transitions to coincide, to give rise to a coupled first order magnetic transition. Physical pressure on the other hand, does not suffer from parasitic effects originating in the substitution itself and thus retains the composition and purity of the sample [1]. Thus hydrostatic pressure provides a clean way of probing the spin-lattice coupling and is useful in elucidating the effects of chemical pressure. Previous studies have demonstrated successfully that the pressure tuning of magnetocaloric effect (MCE) in certain magnetocaloric materials is an effective way of improving magnetic refrigeration [2-3]. Caron *et al* demonstrated the effects of chemical and physical pressure on the magnetic properties of the $Mn_{1-x}Cr_xCoGe$ series of compounds [1]. They compared magnetic and crystallographic data obtained using chemical and physical pressures and they concluded that the magnetocrystalline coupling observed in these compounds were more easily driven by crystallographic than magnetic field changes. It was reported that the orthorhombic TiNiSi-type structure of MnCoGe is a 3d metal-based ferromagnet with a Curie temperature (T_C) of ~345 K While its T_c changes to be 283 K for the TiNiSi-type structure of MnCoGe and a diffusionless crystallographic phase transition from the low-temperature orthorhombic TiNiSi type to the high-temperature hexagonal Ni₂In type of structure at T_{str} ~650 K [4]. Previous investigation on the effects of external pressure on the transition temperatures of MnCoGe using an ac susceptibility method under hydrostatic pressure up to 1.3 GPa. indicates that T_{str} decreases with pressure ($dT_{str}/dP=-116$ K/GPa) [5]. Recently we reported that the substitution of small amount of Ti can significantly reduce the T_{str} and result in larger magnetocaloric effect using magnetic

measurement and neutron diffraction [6]. The major aim of this work is to study the stability of the crystallographic structures of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy under an applied hydrostatic pressure. In this work, we intend to probe the response of the structural transition to the applied hydrostatic pressure. A thorough understanding of this response will be of paramount importance in the design of novel magnetic refrigerants with magnetostructural couplings.

2. Experimental procedure

Polycrystalline $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ ingot was prepared by arc melting the appropriate amounts of Mn (99.9%), Ti (99.999%) powder, Co (99.9%) and Ge (99.999%) chips in an argon atmosphere. During arc melting, a 3% excess Mn over the stoichiometric amount was added to compensate the weight loss of Mn. The polycrystalline ingot was melted five times to achieve good homogeneity. The ingot was then wrapped in tantalum foil, sealed in a quartz ampoule and subsequently annealed at 850°C for 120 h and then quenched in water at room temperature.

The high pressure x-ray powder diffraction experiments on the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy were performed in a diamond anvil cell (DAC). The sample chamber was made from a cavity drilled in the stainless steel gasket preindented to a thickness of 100 μm . The polycrystalline fragments of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy were finely ground and a small amount (less than 1 μg) was loaded into the sample chamber together with two tiny ruby pieces to be used as pressure calibrants. The pressures were measured based on the shifts of the ruby R_1 and R_2 fluorescence lines [7]. A 4:1 methanol-ethanol mixture was loaded additionally into the sample chamber to act as a pressure transmitting medium. The high pressure diffraction studies at room temperature were undertaken using the Powder Diffraction (PD) beamline at the Australian Synchrotron facility in the pressure range from ambient to 10.4 GPa. The monochromatized beam with a wavelength of 0.7742 nm was used. The patterns were collected by a MAR345 image plate detector and converted to a 2θ versus intensity plot using

Fit2D [8]. These patterns were refined using the FULLPROF program to determine the cell parameters [9].

3. Results and discussion

Fig. 1 shows a series of diffraction patterns of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy collected at different pressures. At ambient pressure all peaks can be indexed according to the hexagonal Ni_2In -type structure (space group $P63/\text{mmc}$). This indicated that the temperature for the crystal symmetry change from orthorhombic to hexagonal should shift to below room temperature as confirmed by our neutron study [6]. As can be seen in Fig. 1, with increasing pressure, the peaks shift to the larger angles due to contraction of the lattice. On closer inspection, the peaks appear to start broadening (strain effects) with an increase in pressure. There are no indications of a phase transition and the signatures of the hexagonal phase persist in the entire range of our measurements. This is different from the case detected for MnCoGe [5], $\text{Mn}_{0.93}\text{Cr}_{0.07}\text{CoGe}$ [1] and $\text{Mn}_{0.92}\text{Fe}_{0.06}\text{CoGe}$ [10] where at room temperature and ambient pressure, the compounds exhibit a pure orthorhombic structure [5] or a mixture of orthorhombic and hexagonal structure [1, 10] so the applied pressure can result in a crystal symmetry change from orthorhombic to hexagonal. Based on the fact that a large volume decrease of approximately 3.9% [11-13] in MnCoGe -based compound occurs at T_{str} when the crystal symmetry changes from orthorhombic to hexagonal, this can be easily understand that our sample $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy at room temperature and ambient pressure is already in the hexagonal phase resign (similar volume region).

The application of pressure modifies the structural parameters and Fig. 2 shows the evolution of structural parameters for the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy with pressure. It is clear from Fig. 2 that the lattice parameters a and c , monotonically decrease in the entire range of our measurements. The fact that both lattice parameters a and c exhibit a similar monotonic

pressure dependence, indicates the absence of substantial anisotropy in the compressibility along a and c . The pressure dependence of the volume does not include any discontinuity, confirming that there is no phase transition occurring in the entire range of our measurements.

In an effort to probe further the anisotropy, we investigated the pressure dependence of the c/a ratio, shown in Fig. 3. This figure shows that there is a decrease of c/a ratio with pressure in the entire range of our measurements. The absence of a sudden jump in the c/a ratio with pressure confirms that there is no structural phase transition occurring in the entire range of our measurements.

Unit cell dimensions were derived by Le Bail fitting to the observed powder diffraction patterns by means of the general structure analysis system using FULLPROF. The experimental pressure – volume data for the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy were fitted to a Murnaghan equation of state (EOS) [14]:

$$P = (B_0/B')[(V_0/V)^{B'} - 1] \quad (1)$$

where V_0 , B_0 and B' are the volume, bulk modulus at its first derivative at ambient pressure. The experimental pressure – volume data was also fitted using a third order Birch – Murnaghan EOS shown below:

$$P = 1.5B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}] \times \{1 + 0.75(B' - 4)[(V/V_0)^{-2/3} - 1]\} \quad (2)$$

The bulk modulus (B_0) and its pressure derivative (B') were extracted by fitting the experimentally observed pressure versus volume data to;

- i. the Murnaghan EOS.
- ii. the third order Birch – Murnaghan EOS (using a constrained value of B').
- iii. the third order Birch – Murnaghan EOS (using an unconstrained value of B').

In all three cases, the fitting was done using the computer program EOS - FIT V5.2 [15]. As an input to the program, initial values of $V_0 = 68.14 \text{ \AA}^3$ as well $B_0 = 140 \text{ GPa}$ were used. It should be noted that the extraction of the EOS parameters using the Murnaghan EOS was for comparative purposes only. However, the use of the third order Birch – Murnaghan EOS for the determination of the EOS parameters for the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy is justified since this equation provides an excellent description of the compression of most solids [16-19]. The pressure – volume data has been analysed first by assuming and fixing B' to be 4, and secondly by allowing B' to be 4 to vary during the fitting process. In this case of fixing B' to be 4, this EoS is truncated at second-order in the energy then the coefficient of finite strain f_E must be identical to zero (higher-order terms are ignored) [15]. The value of $B' = 4$ has been experimentally shown to reproduce compression data for a wide variety of substances [20]. The refined values of B_0 and B' are shown in Table 1. In this case, the use of the unconstrained value of B' determined the bulk modulus to be $B_0 = 222.64 \pm 36.9$. The uncertainty in the determined B_0 is too large, therefore we consider the fit with B' fixed at 4, to yield the best value for the bulk modulus which is determined to be $B_0 = 231.72 \pm 7.79$. It also worth noting that the EOS parameters determined using the Murnaghan EOS are a close match to those determined using the third order Birch – Murnaghan EOS (using a constrained value of B').

The variation of the relative volume with pressure data shown in Fig. 4 was fitted using the third order Birch – Murnaghan EOS (using a constrained value of B'). The result of the fit is shown as a solid line in Fig. 4 demonstrating the excellent agreement between the fitted curve and the experimental data.

The application of pressure modifies the structural parameters such as the Mn-Mn interatomic distance of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy. The bond lengths were calculated using the BLOKJE program [21]. Fig. 5 shows that with increasing pressure, the Mn-Mn interatomic distance monotonically decreases up to 10.4 GPa. At ambient pressure the closest distance between Mn-Mn is determined to be 2.644 Å in the Ni_2In -type unit-cell while it changes to 2.552 Å at a pressure of 10.4 GPa. It was reported that, in both orthorhombic and hexagonal structure, the MnCoGe related compounds behave as a typical ferromagnet. For the orthorhombic phase, the larger distance between the dominant Mn–Mn ferromagnetic coupling will lead to the narrower 3d bandwidths and a large exchange splitting between the majority and minority bands then result in the larger moment [22]. On the contrary, the hexagonal phase with shorter Mn-Mn distances has the smaller magnetic moment due to the stronger Mn–Mn ferromagnetic coupling and the resulting wider 3d band. In this study, the reduction in the Mn-Mn distance due to the application of pressure will be expected to lead to a further decrease of magnetic moment as detected for $\text{Mn}_{1-x}\text{Cr}_x\text{CoGe}$ compounds in ref [1].

4. Conclusions

High pressure x-ray diffraction studies were performed on the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy up to a pressure of 10.4 GPa. The hexagonal Ni_2In -type structure (space group P63/mmc) structure is stable in the investigated pressure regime and no phase transition is found to occur. Unit cell parameters were determined and the calculated volumes were found to be well reproduced by the third order Birch – Murnaghan equation of state. The bulk modulus $B_0 = 231.72 \pm 7.79$ GPa has been determined from the observed pressure – volume data. The determination of the EOS parameters and the investigation of the phase stability with pressure of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy are useful guidelines that can be used together with theoretical calculations to predict crystallographic phase transitions.

Acknowledgements

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Table:

EOS	B_0 (GPa)	dB/dP (B')	Comment
Murnaghan	232 ± 7.79	4 (assumed)	B' constrained
3 rd order Birch - Murnaghan	231.72 ± 7.79	4 (assumed)	B' constrained
3 rd order Birch - Murnaghan	222.64 ± 36.9	5.79 ± 7.006	B' unconstrained

Table 1 Equation of state (EOS) parameters for the $Mn_{0.94}Ti_{0.06}CoGe$ alloy.

Figure captions:

Fig. 1. Evolution of powder diffraction patterns for the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy at selected pressures.

Fig. 2. Evolution of structural parameters for the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy with pressure. The dashed line through the data points is a guide to the eye.

Fig. 3. c/a ratio versus pressure for the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy. The dashed line through the data points is a guide to the eye.

Fig. 4. Relative volume of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy as a function of pressure. The solid line represents the Birch-Murnaghan equation of state using the parameters obtained in this study.

Fig. 5. Pressure dependence of the Mn – Mn interatomic distances in the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy. The line serves as a guide to the eye.