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Spin–flip transition of $L1_0$-type MnPt alloy single crystal studied by neutron scattering

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Abstract

Magnetic structure, tetragonality, and the spin–flip transition for an $L1_0$-type MnPt ordered alloy were studied by neutron scattering using a single-crystal specimen. Tetragonality of the lattice showed strong correlation with the spin–flip transition. Although the spin–flip transition looks like a gradual change of the easy axis in the temperature range between 580 and 770 K, two modes of magnon-gap peaks with different energies were observed in this transition temperature range. Thus, the crystal consists of two regions with different anisotropy energies and the volume fractions of these regions with different spin directions change gradually with temperature. The tetragonality and spin–flip transition are discussed using the hard-sphere model for atomic radii of Pt and Mn. The Invar effect of Mn atoms is proposed using high- and low-spin transitions of Mn moments in analogy with the two-γ model of Fe moments in FeNi Invar alloy.

1. Introduction

Since antiferromagnetic MnPt and MnIr alloy thin films with an $L1_0$ (CuAu-I)-type atomic structure are important for application to the pinning material of the ferromagnetic sheets in giant magneto-resistance (GMR) devices, a great amount of data for applications of these materials has piled up in the last decade [1]. However, the basic physical properties of these alloys have not been well understood. The magnetic structures and lattice properties of $L1_0$-type Mn-based equi-atomic alloys were studied in the latter half of 1960. Regarding the magnetic structure of the MnPt alloy, previous authors reported inconsistent results. Andresen *et al*, Pal *et al*, and Kren *et al* reported that the Mn spins couple antiferromagnetically on the *c*-plane, and that the spin axis is parallel to the *c*-axis at room temperature [2–4]. Severin *et al*, however, obtained the result that the Mn spins are within the (0 0 1) plane at room temperature for both quenched and annealed specimens [5]. Thus, the magnetic structure of $L1_0$-type MnPt alloy is still controversial. Furthermore, Pal *et al* and Kren *et al* found a strange temperature variation in the magnetic Bragg peak intensities at high temperature [3, 4]. Although the Mn spins are parallel to the *c*-axis at room temperature, the spin axis lies within the *c*-plane above

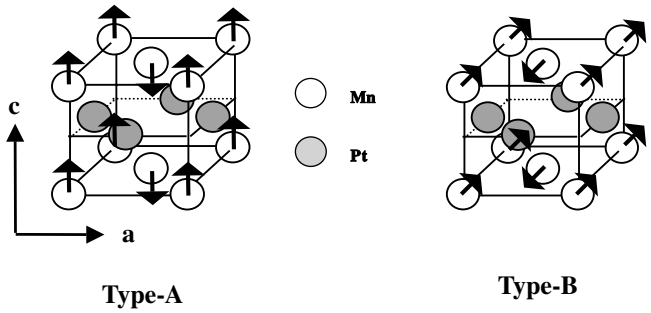

Figure 1. Magnetic structures proposed in previous studies. Type-A: spin axis is parallel to the *c*-axis. Type-B: spin axis is in the *c*-plane.

750 K. The spin–flip transition takes place in the temperature range between 580 and 770 K and the easy axis appears to change continuously from the *c*-axis to the *c*-plane. In the GMR devices, since a ferromagnetic layer is pinned through unidirectional exchange coupling with MnPt film, the change in the spin direction in the MnPt alloy has an essential influence on pinning of the ferromagnetic sheet. Thus, it is important to determine the facts and define the mechanism of gradual spin–flip transition from both viewpoints of fundamental physics and practical applications. All previous authors conducted their studies with powder samples. Since we succeeded in growing a single crystal of the MnPt alloy, we performed neutron scattering experiments on the single crystal to achieve the above-mentioned purpose. In this paper, we report the neutron scattering data on the magnetic structure, temperature dependence of the lattice parameters, and the high-temperature magnetic behaviour for the single-crystal $L1_0$-type MnPt ordered alloy.

2. Experimental details

A single crystal of MnPt ordered alloy with a volume of about 1 cm^3 was grown by the Bridgman method using a furnace with carbon electrodes and then cooled to room temperature in the furnace. Neutron scattering measurements were carried out using the T1-1 triple-axis spectrometer installed in the thermal guide of JRR-3M, Tokai, Japan Atomic Energy Agency (JAEA). The incident neutron wavelength was fixed at 0.254 nm using a pyrolitic graphite filter to eliminate the higher-order contamination. Through these neutron scattering measurements, it was found that our sample was a mono-domain single crystal with a mosaic spread of 1.5° (FWHM), probably due to the large tetragonal lattice distortion ($c/a \sim 0.914$ at room temperature). This factor provides a clear advantage when studying the magnetic structure and other magnetic properties, because the magnetic domain distribution is usually unknown in a multi-domain sample and we have to assume it to be equally distributed to determine the magnetic structure. Although the special thermal treatment for developing the $L1_0$-type chemical order was not performed, the tetragonality of the sample at room temperature shows the same value as the annealed sample of previous studies [5] and guarantees a high degree of atomic order parameter (previous authors reported $S \simeq 0.87(\pm 0.11)$ for the same value of c/a [5]).

3. Experimental results

3.1. Magnetic structure

The magnetic structures reported by previous authors were inconsistent, and are given in figure 1. Andresen *et al* first found the type-A structure at room temperature [2]. The report

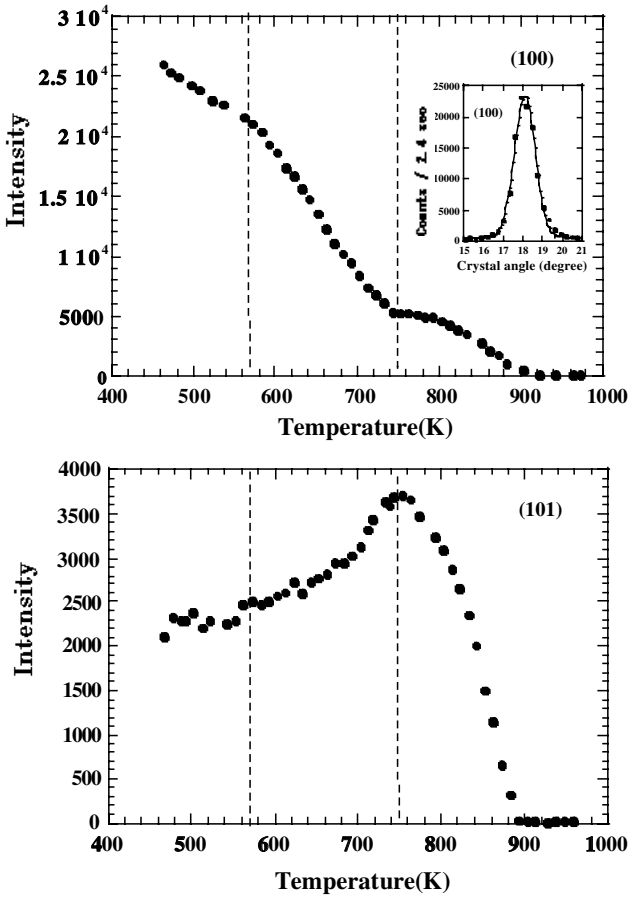

Figure 2. Temperature variations of the (1 0 0) and (1 0 1) magnetic Bragg peak intensities. Dotted lines indicate the start and finish points of the spin–flip transition. Inset shows the line profile of ω-scan at the (1 0 0) magnetic Bragg peak position.

by Kren *et al* demonstrated the existence of a spin–flip transition from a type-A structure to a type-B structure at high temperature [4]. Subsequently, Severin *et al* found that the type-B structure was present even at room temperature [5]. All of these studies used powder samples for neutron scattering experiments. In order to better understand the magnetic structure, our single-crystal sample was set at the [0 1 0] axis perpendicular to the scattering plane. This allowed us to observe the pure magnetic Bragg peaks at the 1 0 0 and 1 0 1 reciprocal lattice positions for both magnetic structures, because nuclear scattering with these indices disappears for the $L1_0$-type chemical order in this condition. Temperature variations of magnetic Bragg peak intensities were studied for these magnetic peaks. Experimental data are given in figure 2. The 1 0 0 magnetic Bragg peak intensity starts decreasing rapidly at around 570 K, and at the same temperature the 1 0 1 Bragg peak intensity starts increasing. Around 750 K, the rapid decreasing of the 1 0 0 peak intensity stops and the 1 0 1 peak shows its maximum intensity. Above this temperature, the magnetic peak intensities show a normal temperature variation up to T_N. Since our sample was a mono-(chemical) domain single crystal, we could determine the magnetic structure more precisely. The calculated magnetic peak intensity ratios $I(1\,0\,0)/I(1\,0\,1)$ for the type-A and type-B structures are 3.88 (T = RT) (3.80 (T = 813 K))

and 1.46 (T = RT) (1.47 (T = 813 K)), respectively[1]. In this calculation, an equal distribution of the magnetic domains with spin axis parallel to the [1 0 0] and [0 1 0] directions in the high-temperature phase was assumed and corrections for the magnetic form factor and the Lorentz factor were performed. The observed values of integrated intensity ratios at RT and 813 K were 3.70 and 1.86, respectively. Thus, the observed intensity ratio in the low-temperature phase is close to that of the type-A structure and in the high-temperature phase is of the type-B structure. This is consistent with the model provided by Kren *et al* [4]. Although the magnetic moments in the high-temperature phase lie on the c-plane (type-B), the direction of the moments on the c-plane is still unknown. In neutron scattering, we cannot distinguish the magnetic domains with the spin axis parallel to the [1 1 0] axis and the equally distributed multi-domain states with spin axis parallel to the [1 0 0] and the [0 1 0] directions.

3.2. Tetragonality

Pal *et al* reported anomalous contraction of c-axis with increasing temperature at high temperature for $L1_0$-type MnPt, MnPd, and MnNi alloys [3]. Since a spin coupling normally has a strong correlation with atomic distance, careful examinations of lattice parameters were performed at various temperatures. The results are given in figure 3. The a-axis expands monotonically with increasing temperature over the entire measurement temperature range. The overall change in the lattice parameter a is consistent with that reported by previous authors. In our data, however, the c-axis starts contracting at about 600 K, nearly coinciding with the temperature at which the 1 0 0 magnetic Bragg peak intensity starts decreasing rapidly and the 1 0 1 peak intensity increases. Thus, the magnetic phase transition has a strong correlation with the tetragonality of the lattice. This point shows a clear contrast to the result given by the previous authors. They reported that there is no direct connection between the anisotropy energy and the lattice dimensions [4].

Assuming the atoms to be hard spheres, the data were analysed using the effective atomic radii of Pt and Mn, R and r, respectively. On the closed pack (1 1 1) plane, the following equations hold:

$$4R = (2)^{1/2}a \qquad \text{and} \qquad 2(R + r) = (a^2 + c^2)^{1/2}.$$

Substituting the experimental values of a and c, we obtain the temperature variation of the effective atomic radii, R and r, as shown in figure 4. The effective atomic radius of Pt (R) increases linearly with temperature. This is due to the thermal expansion and seems to be a normal behaviour. The effective atomic radius of Mn, however, starts shrinking around 600 K, and continues up to T_N as the temperature increases. Thus, within the hard sphere model, the magnetic phase transition is relevant to the shrinkage of the atomic volume of Mn.

3.3. Magnetic anisotropy energy

The magnetic phase transition is a spin–flip transition from the spin axis parallel to the c-axis to the perpendicular direction. However, the transition takes place in a rather wide temperature range between 570 and 750 K. To define the origin of the gradual change of the spin easy axis, microscopic magnetic anisotropy energy was studied through the magnon gap energy.

For an antiferromagnetic substance, magnon energy is generally written as [6]

$$\omega_k = \omega_c[(1 + \omega_A/\omega_c)^2 - \gamma_k^2]^{1/2},$$

[1] Since the tetragonality c/a changes with temperature, the factor $[1 - (\mathbf{K} \cdot \mathbf{e})^2]$ in the magnetic scattering cross section changes with temperature.

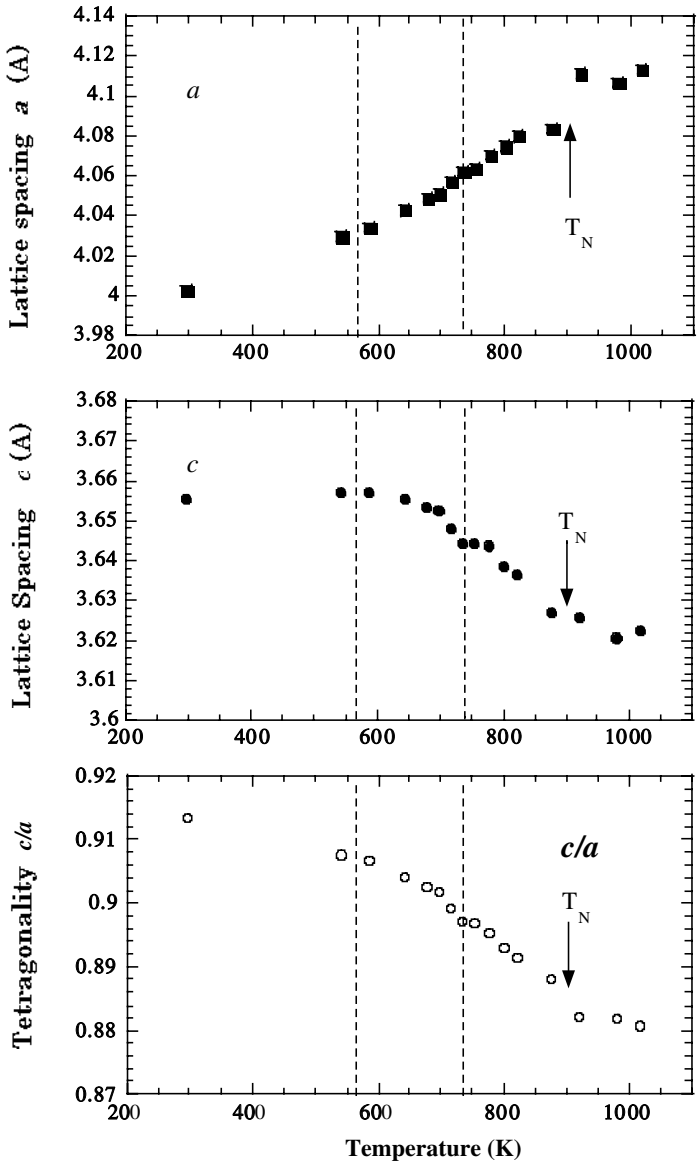

Figure 3. Temperature variations of lattice parameters a and c and the tetragonality c/a.

where $\omega_c = 2\,JzS$, $\omega_A = 2\,\mu_0 H_A$ and $\gamma_k = (1/z)\sum e^{ik\delta}$. H_A is an effective field acting on the sublattice magnetic moments and gives us the crystal anisotropy energy, and z is the number of nearest-neighbour magnetic atoms. If we consider only the nearest-neighbour interaction and at $k = 0$, then $\gamma_k = 1$ and the magnon gap energy at $k = 0$ is given as

$$\omega_{k=0} = \omega_A(1 + 2\omega_c/\omega_A)^{1/2}.$$

Thus, the magnon gap energy at $k = 0$ gives the anisotropy energy.

Experimental data were taken at the 1 0 0 reciprocal lattice point at various temperatures. Observed energy spectra are given in figure 5. At room temperature, an inelastic peak was observed at 7 meV, however a new peak appeared at the low-energy side at 473 K. The new

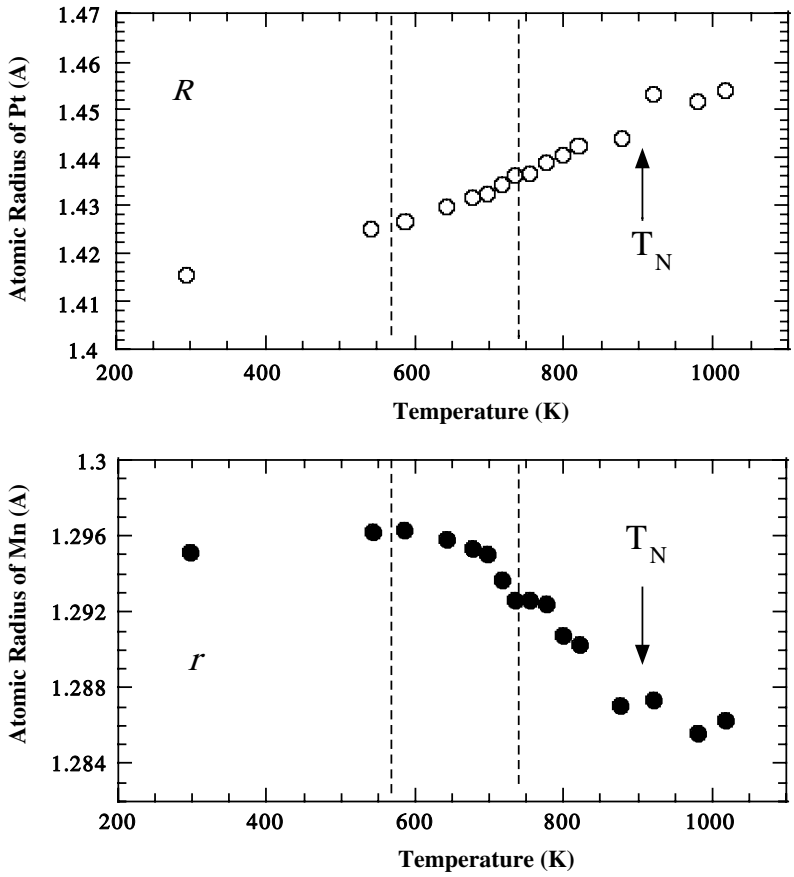

Figure 4. Effective atomic radii of Pt and Mn atoms estimated using the equations in the text.

peak shifts toward the low-energy side with growing intensity as the temperature is increased. Note that the high-energy peak remains unchanged, but the intensity gradually decreases. Thus, there are two excitation peaks in the spectra above 473 K. Remember that the 1 0 0 Bragg peak intensity decreases and the 1 0 1 peak intensity increases in these temperature ranges. If the spin axis gradually tilts from the *c*-axis, the system is a single phase. Then, the anisotropy energy could be uniquely determined, and a single excitation peak would be expected. In our inelastic scattering data, two distinct excitations were observed. Again, remember that we cannot distinguish a mixture of two states with perpendicular spin axes (inhomogeneous model) or a single domain with intermediate spin direction (homogeneous model) from the Bragg peak intensities in neutron scattering measurements. Thus, our data support the inhomogeneous model, in which the spin–flip transition takes place abruptly at separated local area and the volume fraction of each region with different spin direction gradually changes with increasing temperature. In figure 5, the rapid increase in the low-energy peak intensity as the temperature increases might be because of several reasons. As the temperature rises, the volume fraction of the high-temperature phase (with low anisotropy energy) increases, and the temperature factor (the Bose–Einstein distribution factor) increases. Furthermore, neutron scattering intensity is proportional to the reciprocal of the excitation energy.

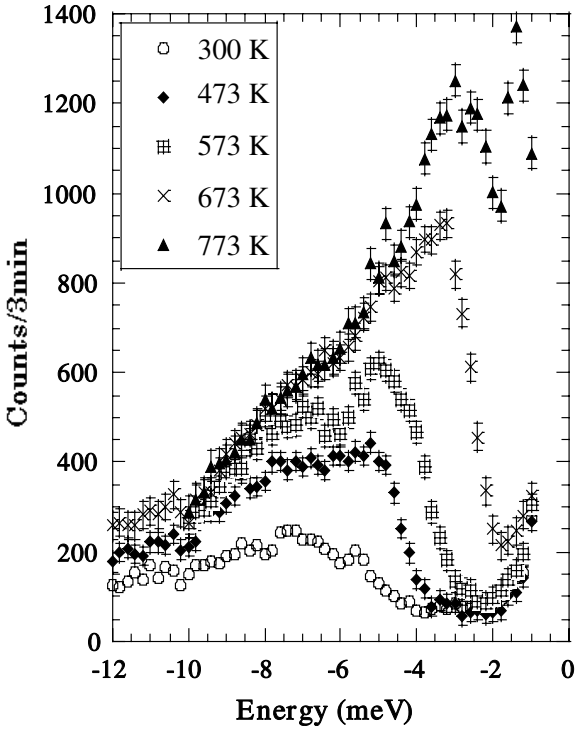

Figure 5. Energy spectra of scattered neutrons obtained at the (1 0 0) Bragg peak position at various temperatures.

4. Discussion

The magnetic structure in the $L1_0$-type MnPt ordered alloy, studied in a single crystal, is consistent with that reported by Pal *et al* and Krěn *et al*, although the Néel temperature of our sample is slightly lower than that of their sample [3, 4]. This inconsistency might be ascribed to the difference between single-crystal and powder samples.

One important difference in our study from that of others is the temperature variation of the *c*-axis. The data of previous studies showed no anomalies at around 600 K, and they concluded that there is no direct connection between the anisotropy energy and the lattice dimensions. However, our data show that the lattice contraction of the *c*-axis starts at around 600 K, which nearly coincides with the temperature at which the 1 0 0 magnetic Bragg peak intensity starts decreasing rapidly and the 1 0 1 peak intensity increases. Thus, the anisotropy energy (spin axis direction) and the lattice contraction have a strong correlation.

According to Pal *et al*, the *c*-axis contraction at high temperature is a common feature for the Mn-based $L1_0$-type alloys MnPt, MnPd, and MnNi, indicating that Mn atoms play a key role in understanding this phenomenon [4]. Within our hard-sphere model, the *c*-axis contraction is relevant to the shrinkage of the Mn atomic radius. The averaged Mn atomic radius shrinks at high temperature, as shown in figure 4. This behaviour reminds us of the famous FeNi Invar alloys. The Invar effect is observed for ferromagnetic face-centred cubic (fcc) FeNi alloys with a concentration of about $Fe_{65}Ni_{35}$. A similar Invar effect is also known for the ordered (Cu_3Au-type) and disordered FePt alloys with a composition of about $Fe_{75}Pt_{25}$. In the two-γ model for the Invar effect, Fe atoms in the fcc structure have two electronic states

which are almost degenerate in energy. At low temperature, Fe atoms are in the high-spin state with large atomic volume. As the temperature increases, Fe atoms transform from the high-spin state to the low-spin state with small atomic volume. Thus, the shrinkage of the volume with increasing temperature compensates the thermal expansion, resulting in an 'invariant' of mean lattice parameters over a wide temperature range [7]. This transition is not a co-operative one but a gradual change extending over a wide temperature range. Since Mn atoms in metallic systems also have states with different atomic volumes and magnetic moments, as is well known in each site of α-Mn, we can propose a similar model for the gradual change of the c-axis contraction of the $L1_0$-type MnPt ordered alloy. In this case, since Mn and Pt planes are alternately piled up along the c-axis, as shown in figure 1, the shrinkage in Mn atomic volume at high temperature leads to the c-axis contraction, as is observed. Recently, we found a similar c-axis contraction at high temperature for the $L1_0$-type FePt ordered alloy [8] in which Fe spins couple ferromagnetically on the c-plane and the spin axis is parallel to the c-axis. However, no spin–flip transition is reported. From the analogy to the well-known Invar effect for the Fe_3Pt alloy, we proposed the same model as that presented here, i.e. the shrinkage of Fe atomic volume at high temperature. In the present measurements, determining the Mn magnetic moment at high temperatures was difficult because of the strong secondary extinction effect of neutron diffraction for a single-crystal specimen. Direct observation of the shrinkage of the Mn magnetic moment at high temperatures, using a powder sample, would be a useful future study.

If we assume the Invar-like phase transition from high- to low-spin states for Mn moments, the explanation of the double-peaked structure and the temperature variation of its magnon gap (anisotropy) energy would be straightforward. At room temperature, most of Mn spins are still in the high-spin state and have rather high anisotropy energy with the spin axis parallel to the c-axis. With increasing temperature, Mn atoms with a low-spin state, which has small anisotropy energy, gradually increase. The easy axis of the Mn spins would be determined by the concentration of high- and low-spin states in the local area, and the spin axis in the area with high concentration of low-spin state would be in the (0 0 1) plane.

Sakuma performed a first-principles calculation of the electronic structure in the $L1_0$-type MnPt ordered alloy using the tight-binding linear muffin-tin orbital (LMTO) method [9]. He showed that the sharp dip in the desnity of states (DOS) at the Fermi level in both spin states stabilizes the collinear type-1 antiferromagnetic structure of the tetragonal MnPt. Unfortunately, only the ground state was discussed, and nothing was reported on the spin–flip transition at high temperature. The calculation showed that the lattice distortion to $c/a < 1$ lowers the electronic energy, but does not have a strong influence on the magnetism. The present data show that the contraction of the c-axis, as temperature increases, strongly correlates with the spin direction and the magnetic anisotropy energy. In the hard-sphere model, since the Pt atoms have a large atomic volume, shrinkage of Mn atomic volume indicates that direct d-electron hopping between Mn atoms is suppressed and that d–d hybridization between Pt and Mn atoms becomes important at high temperatures. Calculations are needed for systems with smaller c/a values, in which the d–d hybridization between Pt and Mn atoms plays an important role.

Umetsu *et al* studied the electrical resistivity and susceptibility of MnPt alloys with approximate equi-atomic compositions [10]. However, no anomalies associated with the spin–flip transition, near the transition temperature, were observed in either resistivity or susceptibility measurements. The susceptibility data reported by Krěn *et al* also did not show any anomalies around the spin–flip transition temperature, although their neutron scattering data showed the spin–flip transition [4]. This is probably due to the very broad phase transition that takes place in the wide temperature range from 500 to 750 K.

5. Conclusion

Using a single-crystal specimen of the $L1_0$-type MnPt alloy, the magnetic structure, tetragonality, spin–flip transition, and anisotropic energy were studied by neutron scattering. The magnetic structure was consistent with that reported by Pal *et al* and Kren *et al* [3, 4]. The c-axis contraction with increasing temperature showed a strong correlation with the gradual spin–flip transition of the spin axis from the c-axis direction to within the c-plane. The magnon-gap spectrum at $k = 0$ showed a double-peaked structure at high temperature, indicating that the sample was composed of two regions with different anisotropy energies. Using a hard-sphere model of atomic radii, these features were discussed as the Invar effect of Mn atoms, by drawing an analogy with the two-γ model of FeNi Invar alloy.

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