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Magnetic anisotropy of $La_{0.75}Sm_{0.25}Mn_2Si_2$ compound

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Abstract

The magnetic anisotropy of the $La_{0.75}Sm_{0.25}Mn_2Si_2$ compound, which has a layered $ThCr_2Si_2$-type crystal structure, has been studied using a quasi-single-crystalline sample. It was found that the compound possesses a strong uniaxial magnetic anisotropy in both magnetically ordered and paramagnetic states. The magnetic anisotropy of the compound is mainly due to the Mn sublattice anisotropy. In the ferromagnetic state at 180 K, the magnetization process is characterized by the magnetic anisotropy constant $K_1 = 6 \times 10^6$ erg cm^{-3}. In the paramagnetic state, a considerable anisotropy of paramagnetic Curie temperature $\Delta\theta_p \approx 35$ K and an appreciable difference between values of the effective magnetic moment measured along the c-axis and in the basal plane, $\Delta\mu_{eff} \approx 0.4\ \mu_B$ per formula unit, has been observed. The natural layered structure of the compound and partial unquenching of the Mn orbital momentum have been considered as possible reasons for the observed strong magnetic anisotropy.

1. Introduction

The RMn_2X_2 compounds (R is a rare-earth metal, X is Si or Ge) crystallize in the layered $ThCr_2Si_2$-type structure (space group $I4/mmm$). Atoms of each sort in the lattice lie within the equivalent separate atomic planes (layers) stacked along the c-axis in the following strong sequence: –Mn–X–R–X–Mn– [1]. Because of the naturally layered structure, the RMn_2X_2 compounds can be considered as unique objects for studying the physical phenomena intrinsic for multilayers and quasi-two-dimensional materials.

At low temperature, the Mn magnetic moments deviate from the c-axis by the angle $\theta \approx 45°$–$60°$, thus providing the ferromagnetic component of the magnetization of an

individual layer along the c-axis and an antiferromagnetic component in the basal plane. The type of interlayer Mn–Mn magnetic ordering depends on intralayer Mn–Mn distance (the a parameter) and does not depend on the interlayer distance (the c parameter). The rearrangement of the magnetic structure occurs at a critical in-plane Mn–Mn distance $d_c \approx 0.285$ nm. For $d_{Mn-Mn} > d_c$, Mn magnetic moments in adjacent layers are ferromagnetically ordered while for $d_{Mn-Mn} < d_c$ antiferromagnetic ordering is observed [1, 2]. For the ferromagnetic compounds, the component of magnetization along the c-axis disappears with increasing temperature up to a critical temperature $T_C \sim 300$ K, while the in-plane antiferromagnetic ordering exists up to much higher temperatures $T_N \sim 400$ K [3, 4]. The origin of various phase transitions in the RMn_2X_2 compounds has remained unclear up to now.

Magnetic anisotropy should strongly affect the formation of magnetic structures in the layered compounds. It is known that for RMn_2X_2 compounds with magnetic rare-earth elements, the magnetic anisotropy at low temperatures ($T < 20$ K) is determined mainly by the anisotropy of the rare-earth sublattice [5]. The Mn sublattice anisotropy has not been properly studied yet. It was shown in our previous study that the Mn sublattice possesses a strong uniaxial magnetic anisotropy in $LaMn_2Si_2$ compound, where lanthanum is a non-magnetic rare-earth element [6]. It was also assumed that magnetic anisotropy can persist at high temperatures in the paramagnetic state. However, it was very difficult to check this assumption, since these studies were performed on aligned powders fixed by epoxy resin.

The purpose of this work is to study magnetic anisotropy for $La_{0.75}Sm_{0.25}Mn_2Si_2$ quasi-single crystals in both ferromagnetically ordered and paramagnetic states. In $La_{0.75}Sm_{0.25}Mn_2Si_2$ compound, d_{Mn-Mn} is very close to the critical distance d_c, and with increasing temperature, the compound exhibits all magnetic structures and magnetic phase transitions intrinsic for RMn_2X_2 compounds [7, 8].

2. Experimental details

The $La_{0.75}Sm_{0.25}Mn_2Si_2$ compound was prepared by induction melting of the initial high-purity elements under an argon atmosphere, followed by annealing at 1273 K for two days. Quasi-single-crystals of the compound in the form of a plate with size ~ 1.5 mm $\times$ 1.5 mm $\times$ 0.8 mm was selected from a massive polycrystalline ingot. According to the x-ray Laue analysis, the tetragonal c-axis was directed perpendicular to the plate plane, while the a axes of separate crystallites were disoriented by a small angle within the basal plane. The crystallites also have the platelet shape with the plate thickness $\sim$10–100 μm.

Magnetic measurements in the temperature range 1.8 K $< T <$ 320 K were performed using an extraction-type magnetometer in magnetic fields up to 70 kOe produced by a superconducting magnet. Measurements at higher temperatures 300 K $< T <$ 700 K in a magnetic field of 10 kOe were performed using a highly-sensitive vibrating sample magnetometer.

3. Results and discussion

Figure 1 shows the temperature dependence of the magnetization for $La_{0.75}Sm_{0.25}Mn_2Si_2$ measured along the c-axis and in the basal plane in a small magnetic field of 50 Oe. The magnetic structures realized in the compounds at various temperatures and determined early from neutron scattering measurements [7] are shown as insets. As seen from figure 1, four different magnetically ordered structures are observed in the $La_{0.75}Sm_{0.25}Mn_2Si_2$ compound. These structures are canted antiferromagnetic AF′, canted antiferromagnetic AF, canted ferromagnetic F, and paramagnetic P (see [7] for more details). Comparing the $M(T)$

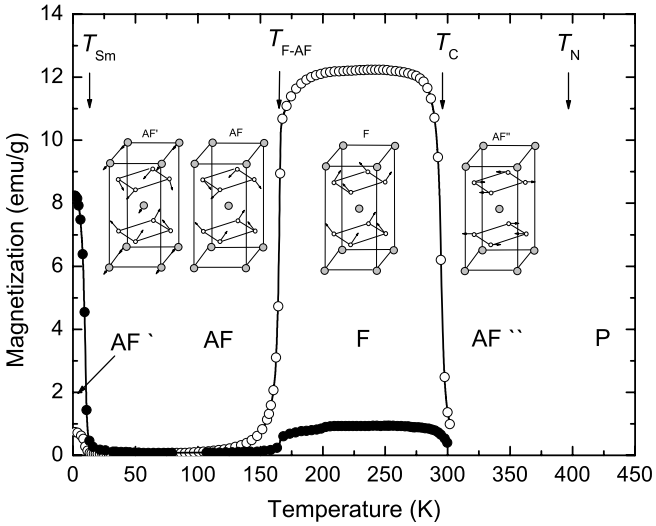

Figure 1. Temperature dependence of magnetization measured on heating parallel to the *c*-axis (open symbols) and in the basal plane (closed symbols) for a quasi-single crystal of $La_{0.75}Sm_{0.25}Mn_2Si_2$. Insets: the magnetic structures for different magnetic states taken from [7]. Only the R atoms (gray spheres) and Mn atoms (white spheres) are shown.

dependences measured in the field applied along the *c*-axis and normal to it (figure 1), one can conclude that the *c*-axis is an easy magnetization direction for the Mn sublattice, while at low temperature the easy-plane anisotropy of the Sm sublattice prevails.

Magnetic states AF′, AF, F and magnetic phase transitions at temperatures T_{Sm}, T_{F-AF} and T_C can be clearly distinguished from the temperature dependence of magnetization of the compounds. In contrast, the AF″ state and the Néel temperature $T = T_N$ are almost undetectable in bulk magnetic measurements [4]. The magnetically ordered AF″ state is evidenced in neutron scattering [4] and Mössbauer experiments [3]. Recently, anomalies were found on the temperature dependence of the heat capacity [9] and the thermal expansion coefficient [10], which were attributed to the AF″–P magnetic phase transition.

Figures 2(a) and (b) show magnetization curves for $La_{0.75}Sm_{0.25}Mn_2Si_2$ compound in the ferromagnetic F state measured along the *c*-axis and in the basal plane at different temperatures. The magnetization curves are typical of an anisotropic uniaxial ferromagnet with the easy *c*-axis. When the field is applied along the *c*-axis, the magnetization saturates in small magnetic field $H \sim 1$ kOe, which corresponds to the demagnetization field of the sample. In the basal plane, the magnetization reaches saturation in considerably higher magnetic fields; the anisotropy field decreases with increasing temperature. The observed high-field susceptibility χ_p is connected with the proximity of the measurement temperatures to the Curie temperature $T_C = 294$ K.

Formation of the canted ferromagnetic structure within the Mn layer is considered to be due to a competition of antiferro-and ferromagnetic in-plane Mn–Mn exchange interactions. These interactions are so strong that the canting angle θ remains almost unchanged in applied magnetic fields [6]. This gives an opportunity to consider $La_{0.75}Sm_{0.25}Mn_2Si_2$ compound in the F state as a collinear ferromagnet with spontaneous magnetization equal to the value of projection of the Mn magnetic moment on the *c*-axis. The expression for free energy of an anisotropic ferromagnet in a magnetic field directed normal to the easy *c*-axis is the sum of the Zeeman energy E_H and magnetic anisotropy energy E_A. Considering only two anisotropy

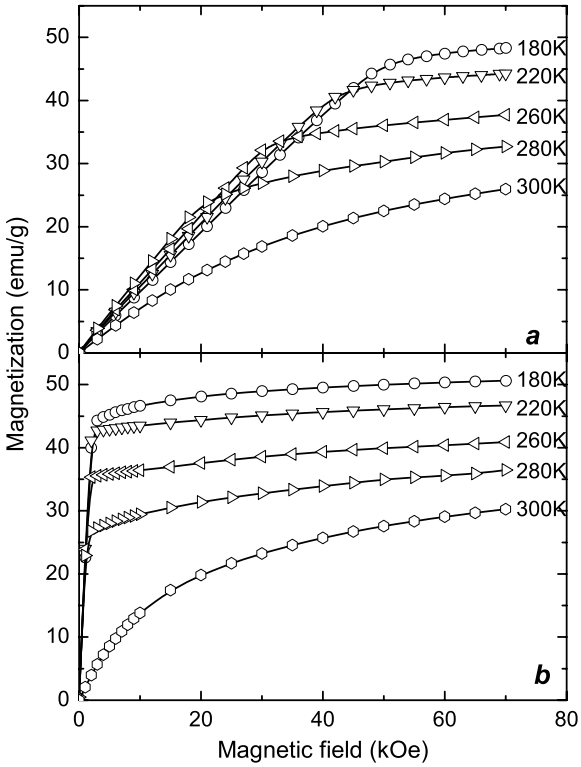

Figure 2. Magnetization curves for $La_{0.75}Sm_{0.25}Mn_2Si_2$ measured at different temperatures in the basal plane (a) and along the *c*-axis (b) in the ferromagnetic F state.

constants, the free energy may be presented as:

$$E = E_{\mathrm{H}} + E_{\mathrm{A}} = -M_{\mathrm{S}} H \sin(\phi) + K_1 \sin^2(\phi) + K_2 \sin^4(\phi) + \cdots, \tag{1}$$

where K_1 and K_2 are magnetic anisotropy constants, M_{S} is the spontaneous magnetization and ϕ is the angle between the magnetization vector and the magnetic field direction. Minimization of (1) with respect to the angle ϕ gives the equilibrium angle ϕ_{e}. The magnetization curve for the field applied in the basal plane is described as follows:

$$M_{\perp}(H) = M_{\mathrm{S}} \cos(\phi_{\mathrm{e}}) + \chi_{\mathrm{p}} H, \tag{2}$$

where χ_{p} is the high-field susceptibility measured in magnetic fields applied along the *c*-axis. We determined the values of the anisotropy constants K_1 and K_2 by fitting the calculated magnetization curves to the experimental ones measured in the basal plane.

Figure 3 shows the temperature dependence of the anisotropy constants K_1, K_2 and the magnetic anisotropy field $H_{\mathrm{a}} = (2K_1 + 4K_2)/M_{\mathrm{S}}$ for the $La_{0.75}Sm_{0.25}Mn_2Si_2$ compound. For comparison, we show also the dependences $K_1(T)$, $K_2(T)$, and $H_{\mathrm{a}}(T)$ for the $LaMn_2Si_2$ compound obtained early [6]. As can be seen from figure 3, the anisotropy constants and magnetic anisotropy field values for $La_{0.75}Sm_{0.25}Mn_2Si_2$ are close to those for the $LaMn_2Si_2$ compound where rare-earth ions are non-magnetic. Therefore, we can conclude that at temperatures $T > T_{\mathrm{Sm}}$ the Sm sublattice does not give an appreciable contribution to the anisotropy of the $La_{0.75}Sm_{0.25}Mn_2Si_2$ compound, whereas the Mn sublattice anisotropy is quite high.

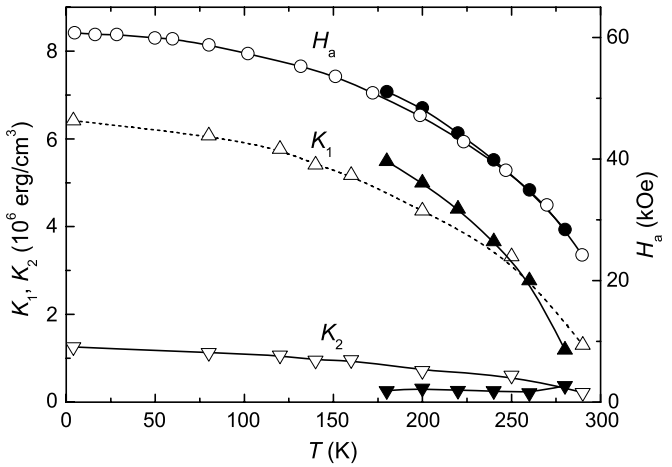

Figure 3. Temperature dependence of the magnetic anisotropy constants K_1, K_2, and the magnetic anisotropy field H_a for $La_{0.75}Sm_{0.25}Mn_2Si_2$ (closed symbols) and for $LaMn_2Si_2$ [6] (open symbols).

Let us analyze the influence of magnetic anisotropy on the F–AF′ magnetic phase transition at $T = T_C$, considering the transition to be of second-order type, similar to that of $LaMn_2Si_2$ [6]. Using the theory of thermodynamic coefficients, we obtain the following expressions for magnetization curves measured along ($M_\parallel$) and perpendicular ($M_\perp$) to the c-axis near T_C:

$$2\alpha(T - (T_C + K_1'/\alpha)) + 4\beta M_\parallel^2 = H/M_\parallel \tag{3}$$

$$2\alpha(T - T_C) + 4\beta M_\perp^2 = H/M_\perp, \qquad (H \geqslant H_a), \tag{4}$$

where α and β are thermodynamical coefficients, and K_1' is a normalized anisotropy constant [6].

Shown in figure 4 are temperature dependences of the α coefficient determined in magnetic fields applied both along the c-axis and in the basal plane. As seen from figure 4, for the $La_{0.75}Sm_{0.25}Mn_2Si_2$ compound a 'shift' of the Curie temperature is observed, which is proportional to the K_1' value. The difference between Curie temperatures measured along the c-axis and in the basal plane, $K_1'/\alpha \approx 11$ K is close to that previously obtained for the $LaMn_2Si_2$ compound value $K_1'/\alpha \approx 9$ K [6].

In figure 5 we show temperature dependences of reciprocal paramagnetic susceptibility for a $La_{0.75}Sm_{0.25}Mn_2Si_2$ quasi-single crystal measured along the c-axis $\chi_\parallel^{-1}(T)$ and in the basal plane $\chi_\perp^{-1}(T)$, and for polycrystalline sample $\chi_{poly}^{-1}(T)$. Solid lines represent temperature dependences of reciprocal paramagnetic susceptibility obtained by fitting the experimental data to the well-known modified Curie–Weiss law:

$$\chi = \chi_0 + \frac{C}{T - \theta_p}, \tag{5}$$

where C is the Curie–Weiss constant, θ_p is the paramagnetic Curie temperature, and χ_0 is temperature-independent contribution to the magnetic susceptibility. As seen from figures 5, the paramagnetic susceptibility strongly depends on the direction of the measurement. At high temperatures $T > 450$ K, the temperature dependences of $\chi_\parallel^{-1}(T)$, $\chi_\perp^{-1}(T)$ and $\chi_{poly}^{-1}(T)$ obey the Curie–Weiss law. With decreasing temperature, deviations of the experimental $\chi_\parallel^{-1}(T)$, $\chi_\perp^{-1}(T)$ and $\chi_{poly}^{-1}(T)$ dependences from the Curie–Weiss law are observed. For polycrystalline

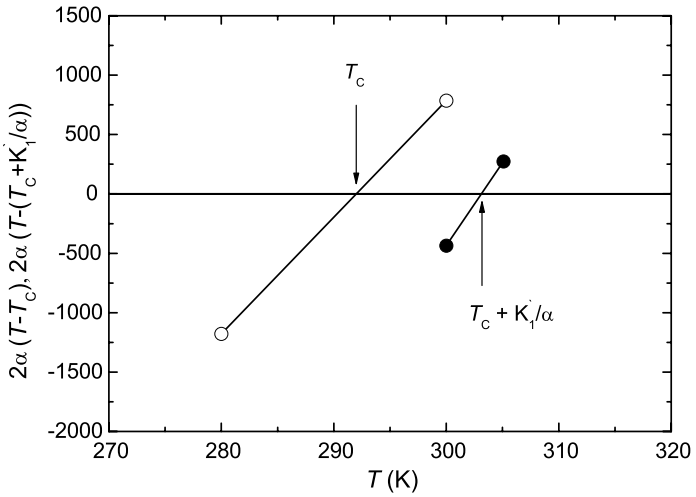

Figure 4. Temperature dependence of thermodynamical coefficients for $La_{0.75}Sm_{0.25}Mn_2Si_2$ measured along the *c*-axis (closed symbols) and in the basal plane (open symbols).

samples, the $\chi^{-1}_{\rm poly}(T)$ dependence practically coincides with that calculated for the compound with a uniaxial anisotropy:

$$\chi^{-1}_{\rm poly} = (\tfrac{1}{3}(\chi_{\parallel} + 2\chi_{\perp}))^{-1}. \tag{6}$$

The deviation from the Curie–Weiss law is considered to be the only method of registration of critical temperature $T_{\rm N}$ of the AF″–paramagnetic phase transition from bulk magnetic measurements [4]. Therefore, it is especially interesting to analyze the differences in behavior of deviation from the Curie–Weiss law $\Delta\chi^{-1}(T) = \chi^{-1}_{\rm CW}(T) - \chi^{-1}(T)$ (where $\chi^{-1}_{\rm CW}(T)$ is calculated using expression (5) and $\chi^{-1}(T)$ is the experimental dependence) observed for polycrystalline and quasi-single-crystalline samples (figure 6). As can be seen from figures 5 and 6, when the field is applied in the basal plane, the deviation from the Curie–Weiss law starts at $T_{\perp} \sim 405$ K, which coincides with the $T_{\rm N}$ temperature determined from non-magnetic measurements [7, 10]. Below this temperature, a decrease of $\Delta\chi_{\perp}$ (increase of $1/\Delta\chi_{\perp}$) occurs. For the polycrystalline sample, the deviation also starts at $T_{\rm N} = 405$ K, however, the value of this deviation is much smaller (figures 5 and 6). When measuring along the *c*-axis, the deviation from the Curie–Weiss law starts at temperature $T_{\parallel} \sim 444$ K which is higher than the $T_{\rm N}$ temperature. At this temperature, a decrease of $\Delta\chi_{\parallel}$ (increase of $1/\Delta\chi_{\parallel}$) occurs (figures 5 and 6), in contrast to the deviations observed in the basal plane and for the polycrystalline sample. The difference in values of $T_{\perp}$ and $T_{\parallel}$ temperatures can be considered as an influence of the magnetic anisotropy on the temperature range of the existence of the AF″ state.

In table 1, the values of the paramagnetic Curie temperature $\theta_{\rm p}$, effective magnetic moment $\mu_{\rm eff}$, and χ_0 obtained by fitting the experimental $\chi^{-1}(T)$ dependences to the modified Curie–Weiss law (5) are shown for the quasi-single crystal and polycrystalline sample of $La_{0.75}Sm_{0.25}Mn_2Si_2$. The difference between $\theta_{\rm p}$ temperatures measured along the *c*-axis and in the basal plane reaches 35 K. Higher values of the paramagnetic Curie temperature determined from measurements along the *c*-axis, $\theta_{\parallel} = 336$ K, in comparison with that in the basal plane $\theta_{\perp} = 301$ K, indicate that a strong uniaxial anisotropy with easy *c*-axis persists in these compounds even in the paramagnetic state. The values of the effective magnetic moment are close to the typical values of the Mn effective magnetic moment determined in other RMn_2X_2 compounds [1]. As can be seen from table 1, a small difference between $\mu_{\rm eff}$ measured along

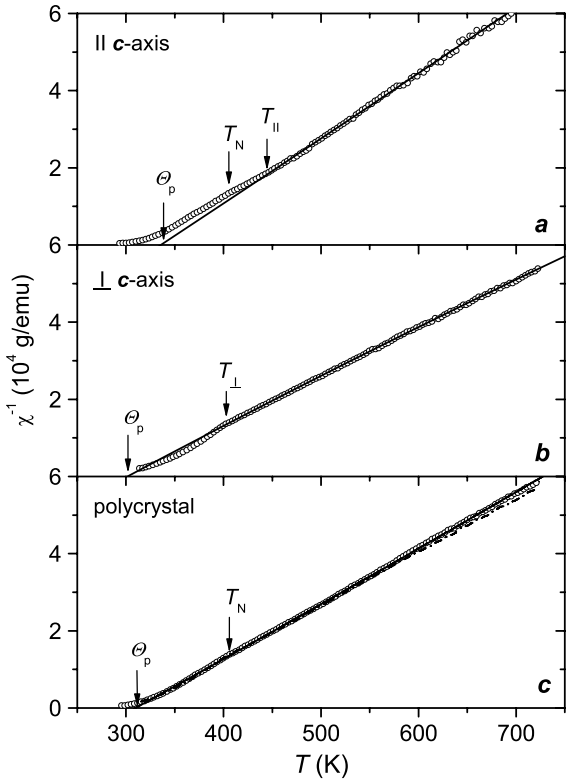

Figure 5. Temperature dependence of the reciprocal paramagnetic susceptibility $\chi^{-1}(T)$ for $La_{0.75}Sm_{0.25}Mn_2Si_2$ along the c-axis (a), in the basal plane (b) and for polycrystalline sample (c). Experimental data (symbols), data calculated by the modified Curie–Weiss law (line), and data calculated for the polycrystalline sample using expression (6) (dashed line) are shown.

Table 1. Values of the paramagnetic Curie temperature θ_p, the effective magnetic moment μ_{eff}, and χ_0 constant for quasi-single crystalline and polycrystalline samples of $La_{0.75}Sm_{0.25}Mn_2Si_2$.

	θ_p (K)	μ_{eff} (μ_B/f.u.)	μ_{eff} [a] (μ_B/Mn)	χ_0 (emu mol^{-1})
Polycrystalline sample	310	4.20	2.95	-1.46×10^{-4}
$\parallel$ c-axis	336	3.84	2.70	-0.62×10^{-4}
$\perp$ c-axis	301	4.27	3.01	$+3.12 \times 10^{-4}$

[a] Values of μ_{eff} on Mn atom were calculated on the assumption that for Sm ion $\mu_{eff} = 0.84\mu_B$/Sm.

the c-axis and in the basal plane exists. The value of μ_{eff} is higher in the basal plane for $\sim$0.43 μ_B/f.u. (formula unit).

The obtained results show the existence of strong uniaxial magnetic anisotropy of the Mn sublattice in the $La_{0.75}Sm_{0.25}Mn_2Si_2$ compound. The Sm sublattice in the compound has an easy-plane anisotropy and appears only at low temperatures $T < T_{Sm}$ when Sm magnetic moments are ferromagnetically ordered. It seems that the strong anisotropy of the Mn sublattice is intrinsic for all RMn_2X_2-type compounds. A strong magnetocrystalline anisotropy and anisotropy of paramagnetic Curie temperature are frequently observed in two types of the compounds: first, in the compounds based on the 4f and 5f metals with localized f-electron shells and unquenched orbital moments; second, in non-metallic compounds based

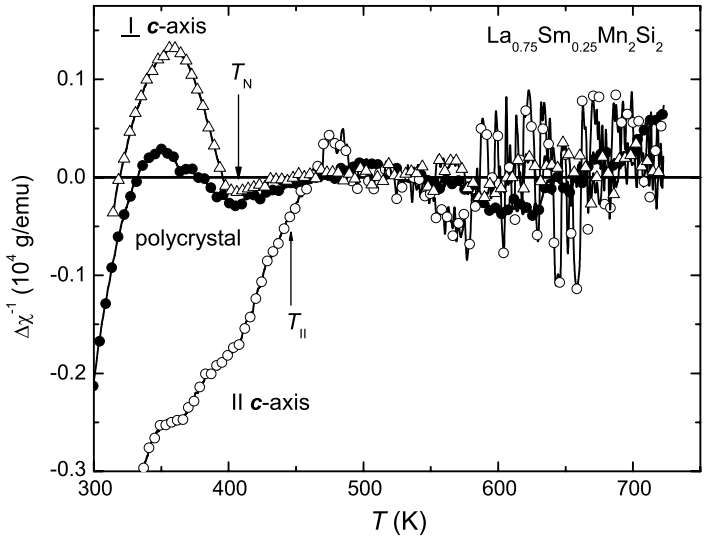

Figure 6. Temperature dependence of the difference of reciprocal paramagnetic susceptibility from the Curie–Weiss law $\Delta\chi^{-1}(T)$ for $La_{0.75}Sm_{0.25}Mn_2Si_2$ measured along the *c*-axis (open circles), in the basal plane (open triangles), and for a polycrystalline sample of $La_{0.75}Sm_{0.25}Mn_2Si_2$ (closed circles).

on 3d transition metals. In the latter case, 3d ions, like f ions, have non-zero orbital momentum. For the case of metallic alloys and intermetallic compounds based on 3d elements, magnetocrystalline anisotropy and anisotropy of paramagnetic Curie temperature are usually small because of a quenching of the orbital momentum. The strong anisotropic effects observed for the Mn sublattice in the $La_{0.75}Sm_{0.25}Mn_2Si_2$ compound may be caused by both partial unquenching of the orbital momentum of manganese and the naturally layered crystal structure of the compound. For example, a strong magnetic anisotropy connected with unquenching of the orbital momentum of Co and Mn was observed in YCo_5 [11] and MnBi [12] compounds. It is also known that for multilayered films based on 3d transition metals, the magnetic anisotropy can be as much as a factor 10 larger than that for bulk materials [11]. As possible experiments to clarify the nature of the strong magnetic anisotropy of Mn in the RMn_2X_2 compound, one could consider investigation of the anisotropy of the *g*-factor.

4. Conclusion

The studies of the magnetic anisotropy of the $La_{0.75}Sm_{0.25}Mn_2Si_2$ quasi-single crystal performed in this work show that the Mn sublattice in RMn_2X_2 compounds with naturally layered crystal structure possesses strong uniaxial magnetic anisotropy. The strong magnetic anisotropy appears not only in the ferromagnetic state, but also at F–AF″, AF″–P magnetic phase transitions and even in the paramagnetic state. At F–AF′, AF″–P magnetic phase transitions, strong differences between critical temperatures of the transitions measured parallel to the *c*-axis and in the basal plane are observed (11 K and 39 K, respectively). The difference between paramagnetic Curie temperatures measured parallel to the *c*-axis and in the basal plane reaches 35 K. In all cases, the values of critical temperatures measured parallel to the *c*-axis are higher than those measured in the basal plane, which indicate the existence of strong uniaxial anisotropy with the easy *c*-axis. The strong anisotropy of the Mn sublattice in the

RMn_2X_2 compound may be connected with the naturally layered crystal structure and with partial unquenching of Mn orbital angular momentum.

Acknowledgments

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