Effect of Pressure on the Curie Point of $Cr_{1-\delta}Te$ System with the Pseudo-NiAs-Type Structure

By

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Pressure effect on the Curie temperature in $Cr_3\square Te_4$ (quenching temperature 1000 °C) with the partially disordered phase of MLD and in $Cr_7\square Te_8$ (1000 °C) with the disordered phase of MLD, and in $Cr_7\square Te_8$ (400 °C) with the ordered phase have been supplementarily investigated by the electrical resistivity measurements and the magnetic induction method, in addition to the previous works. The shifting rates in T_C with increase of hydrostatic pressures up to 5 kbar were determined as: $dT_C/dP = -(5.9 \pm 0.1)$ deg/kbar and $dT_C/dP = -(6.3 \pm 0.1)$ deg/kbar for $Cr_3\square Te_4$ (1000 °C) by the magnetic induction and the electrical resistivity measurements, respectively, and $dT_C/dP = -(6.9 \pm 0.4)$ deg/kbar for $Cr_7\square Te_8$ (1000 °C), $dT_C/dP = -(5.3 \pm 0.2)$ deg/kbar for $Cr_7\square Te_8$ (400 °C) by the electrical resistivity measurements. Little difference in T_C at atmospheric pressure and in the pressure effect on T_C have been observed between $Cr_3\square Te_4$ (1000 °C) and $Cr_3\square Te_4$ (cooled slowly), unlike in the case of $Cr_7\square Te_8$. The magnetic exchange interaction in the MLD-type compound $Cr_{1-\delta}Te$ is also discussed.

Der Druckeinfluß auf die Curietemperatur in $Cr_3\square Te_4$ (Temperungstemperatur 1000 °C) mit partiell fehlgeordneter MLD-Phase und $Cr_7\square Te_8$ (1000 °C) mit fehlgeordneter MLD-Phase und in $Cr_3\square Te_4$ (400 °C) mit geordneter Phase wurde zusätzlich zu früheren Messungen mit elektrischen Widerstandsmessungen und der magnetischen Induktionsmethode ergänzend untersucht. Die Verschiebungsraten in T_C mit ansteigendem, hydrostatischem Druck bis 5 kbar wurde zu $dT_C/dP = -(5,9 \pm 0,1)$ grd/kbar und $dT_C/dP = -(6,3 \pm 0,1)$ grd/kbar für $Cr_3\square Te_4$ (1000 °C) durch magnetische Induktion bzw. elektrische Widerstandsmessung und $dT_C/dP = -(6,9 \pm 0,4)$ grd/kbar für $Cr_7\square Te_8$ (1000 °C) und $dT_C/dP = -(5,3 \pm 0,2)$ grd/kbar für $Cr_7\square Te_8$ (400 °C) durch elektrische Widerstandsmessungen bestimmt. Im Gegensatz zu $Cr_3\square Te_4$ wurden kleine Differenzen in T_C bei Atmosphärendruck und im Druckeinfluß zwischen $Cr_3\square Te_4$ (1000 °C) und $Cr_7\square Te_8$ (langsam abgekühlt) beobachtet. Die magnetische Austauschwechselwirkung in der MLD-Verbindung $Cr_{1-\delta}Te$ wird ebenfalls diskutiert.

1. Introduction

The nonstoichiometric pseudo-NiAs-type compound $Cr_{1-\delta}Te$ is known to have various types of Cr-vancancy arrangements which are introduced by changing the thermal treatment. The crystal structure of $Cr_7\square Te_8$ was studied by Hashimoto and Yamaguchi [1], who reported that $Cr_7\square Te_8$ (1000 °C) with the disordered phase of magnetic lattice defects (MLD) has a hexagonal structure and $Cr_7\square Te_8$ (400 °C) with the ordered phase a monoclinic one. The ordered phase in $Cr_3\square Te_4$ with the monoclinic structure, and both the ordered and disordered phases in $Cr_7\square Te_8$ were previously investigated [2, 3]. The $Cr_3\square Te_4$ sample quenched from 1000 °C is supposed to have the partially disordered phase. The crystal and magnetic structures for the ordered phases of $Cr_3\square Te_4$ and $Cr_7\square Te_8$ are shown in Fig. 1 and 2, respectively.

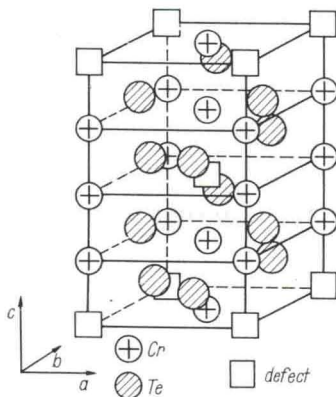[1]) On leave from Faculty of Engineering, Keio University, Yokohama-shi.

Fig. 1. Unit cell and magnetic structure for the ordered phase of $Cr_3\Box Te_4$
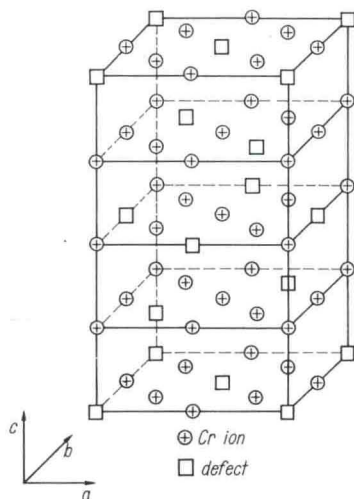
Fig. 2. Unit cell and magnetic structure for the ordered phase of $Cr_7\Box Te_8$ (400 °C). Te atoms are omitted

Recently Andresen [4] has studied the magnetic structure in slowly cooled compound $Cr_{1-\delta}Te$, corresponding to compositions Cr_2Te_3, Cr_3Te_4, and Cr_5Te_6 by neutron diffraction, and estimated the Curie temperatures as 182 ± 2, 325 ± 2, and 327 ± 2 °K, respectively.

In the previous works [2, 3], the pressure effects of T_C of $Cr_3\Box Te_4$ (cooled slowly), and $Cr_7\Box Te_8$ (1000 °C), (400 °C) were investigated, and had negative values. In the molecular field model a large number of exchange chains of these MLD-type compounds are interrupted by MLD in the crystal lattice. Accordingly the Curie temperatures of these compounds were expected to be lower in comparison with that of the non-MLD-type compound CrTe. However, there was no remarkable difference in the observed Curie temperatures. This phenomenon could not be explained by the volume effect of the exchange integral in T_C with $dT_C/dP < 0$. Moreover, the different values in T_C and dT_C/dP were observed between $Cr_7\Box Te_8$ (1000 °C) and $Cr_7\Box Te_8$ (400 °C). Similar results are also expected between $Cr_3\Box Te_4$ (1000 °C) and $Cr_3\Box Te_4$ (cooled slowly). Therefore, it is significant to measure the pressure effect on T_C in $Cr_3\Box Te_4$ (1000 °C) and to compare it with that for $Cr_3\Box Te_4$ (cooled slowly). We also investigated the influence of MLD introduced by changing the nonstoichiometric parameter δ to the pressure effect on T_C in the MLD-type compound $Cr_{1-\delta}Te$.

In this paper, the pressure effects for $Cr_3\Box Te_4$ (1000 °C) and $Cr_7\Box Te_8$ (1000 °C), (400 °C) were determined by both the electrical resistivity measurements and the magnetic induction method at hydrostatic pressures up to 5 kbar.

2. Experimental Methods

The $Cr_3\Box Te_4$ and $Cr_7\Box Te_8$ samples were prepared from chromium and tellurium powders (99.99% purity for each). Thermal treatments of the samples were the same as in the previous papers [2, 3]. These samples were identified by X-ray diffraction pattern in $Cr_3\Box Te_4$ (1000 °C) showed the monoclinic structure like in $Cr_3\Box Te_4$ (cooled slowly). However, a reflection (002) observed for $Cr_3\Box Te_4$ (cooled slowly) was not obtained for $Cr_3\Box Te_4$ (1000 °C). This result

means that the sample $Cr_3\square Te_4$ (1000 °C) is indicated to have the partially disordered phase of MLD. In $Cr_7\square Te_8$ the crystal structures were confirmed to be those reported by Hashimoto and Yamaguchi [1].

The pressure effects on T_C for $Cr_3\square Te_4$ (1000 °C) were determined by the magnetic induction method [2] and by the electrical resistivity measurements, and for $Cr_7\square Te_8$ in both the disordered and ordered phases by the electrical resistivity measurements. The Curie temperatures of $Cr_3\square Te_4$ (1000 °C) and $Cr_3\square Te_4$ (cooled slowly) were also determined by relative magnetization at atmospheric pressure.

3. Experimental Results

3.1 $Cr_3\square Te_4$

The lattice parameters for $Cr_3\square Te_4$ (1000 °C) were determined by X-ray analysis; the results were nearly the same as those for $Cr_3\square Te_4$ (cooled slowly) [2].

The relative magnetization for $Cr_3\square Te_4$ (1000 °C) was observed at atmospheric pressure in a magnetic field at 400 Oe, and the Curie temperature was determined as 326 °K in Fig. 3. The Curie temperature of $Cr_3\square Te_4$ (cooled slowly) was also determined as 326 °K. These results are shown in Table 1.

The temperature dependence of magnetic induction and electrical resistivity for $Cr_3\square Te_4$ (1000 °C) at hydrostatic pressures are shown in Fig. 4 and 5, respectively. Electrical resistivity shows a Γ-type anomaly with a kink at T_C, which also appears in both phases of $Cr_7\square Te_8$. The pressure shifts in T_C for $Cr_3\square Te_4$ (1000 °C) by both measurements are shown in Fig. 6 together with those for $Cr_3\square Te_4$ (cooled slowly) [2]. The shifting rates are tabulated in Table 2. The pressure effect on T_C for $Cr_3\square Te_4$ (1000 °C) is similar to that for $Cr_3\square Te_4$ (cooled slowly).

The variation of electrical resistivity ϱ for $Cr_3\square Te_4$ (1000 °C) as a function of pressure in isothermal measurements is shown in Fig. 7. The value of ϱ at room temperature and atmospheric pressure is about 1.5×10^{-3} Ωcm. Electrical resistivity shows a kink at 4.2 kbar in the isotherm at 297 °K, the transition point from a ferromagnetic to a paramagnetic region, which is regarded as the
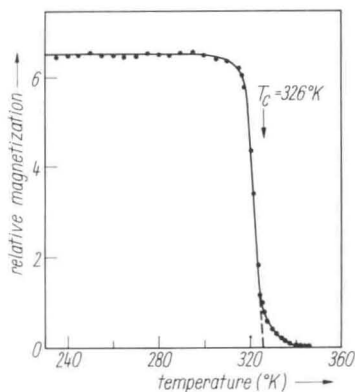

Fig. 3. Temperature dependence of relative magnetization at 400 Oe of $Cr_3\square Te_4$ (1000 °C) at atmospheric pressure

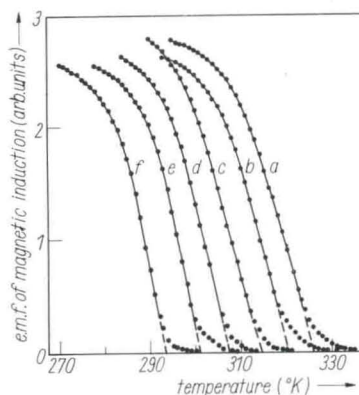Fig. 4. Temperature dependence of magnetic induction of $Cr_3\square Te_4$ (1000 °C) at hydrostatic pressures: (a) 0; (b) 0.85; (c) 2.00; (d) 3.05; (e) 4.25; (f) 5.55 kbar
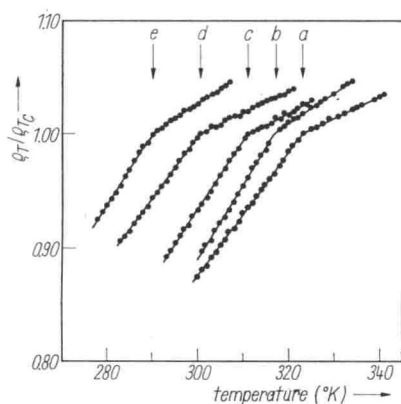
Fig. 5. Temperature dependence of electrical resistivity of $Cr_3\square Te_4$ (1000 °C) at hydrostatic pressures. The electrical resistivity values are normalized to the value at the Curie temperature at each pressure. (a) 0; (b) 1.0; (c) 1.95; (d) 3.55; (e) 5.15 kbar
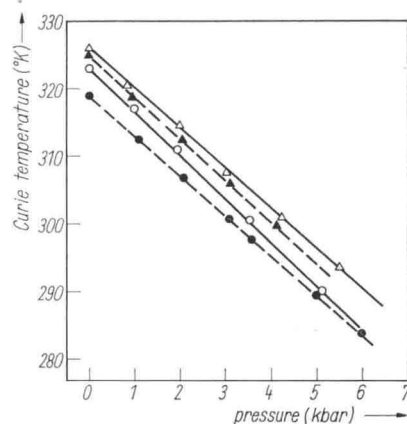
Fig. 6. Pressure dependence of the Curie temperature of $Cr_3\square Te_4$ (1000 °C) and $Cr_3\square Te_4$ (cooled slowly). ○, △: for $Cr_3\square Te_4$ (1000 °C), ●, ▲: for $Cr_3\square Te_4$ (cooled slowly). Triangles and circles represent the results obtained by magnetic induction and electrical resistivity measurements, respectively

Table 1

The Curie temperatures of both phases in $Cr_7\square Te_8$ and $Cr_3\square Te_4$ observed by each method at atmospheric pressure

method	T_C (°K)			
	$Cr_3\square Te_4$ (1000 °C)	$Cr_3\square Te_4$ (cooled slowly)	$Cr_7\square Te_8$ (1000 °C)	$Cr_7\square Te_8$ (400 °C)
relative magnetization	326*)	326*)	343	332
magnetic induction	326*)	325	343	329
electrical resistivity	323*)	319	344*)	332*)

*) present work

Table 2

The shifting rates in T_C observed by different methods

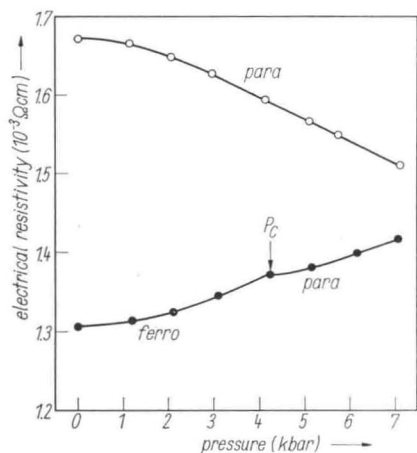| method	dT_C/dP (deg/kbar)			
	$Cr_3\square Te_4$ (1000 °C)	$Cr_3\square Te_4$ (cooled slowly)	$Cr_7\square Te_8$ (1000 °C)	$Cr_7\square Te_8$ (400 °C)
magnetic induction	-5.9 ± 0.1*)	-6.2 ± 0.4	-6.3 ± 0.2	-5.6 ± 0.4
electrical resistivity	-6.3 ± 0.1*)	-5.9 ± 0.3	-6.9 ± 0.4*)	-5.3 ± 0.2*)

*) present work

Fig. 7. Pressure dependence of electrical resistivity of $Cr_3\square Te_4$ (1000 °C) in the isotherms at 335 (○) and 297 °K (●)

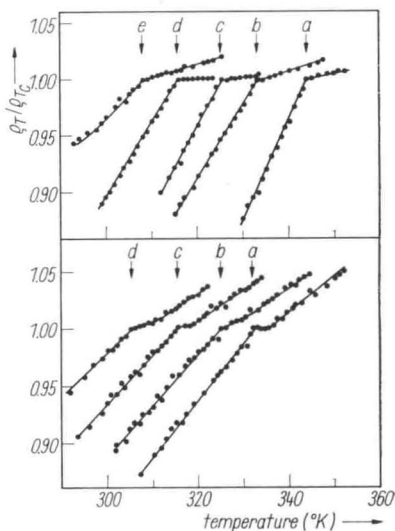Fig. 8. Temperature dependence of electrical resistivity of $Cr_7\square Te_8$ (1000 °C) and $Cr_7\square Te_8$ (400 °C) at different hydrostatic pressures. The electrical resistivity values are normalized to the value at the Curie temperature at each pressure. — Upper plot (1000 °C): (a) 0; (b) 1.50; (c) 2.45; (d) 4.15; (e) 5.10 kbar. Lower plot (400 °C): (a) 0; (b) 1.45; (c) 3.25; (d) 5.10 kbar

transition pressure P_C, which implies that the Curie temperature at 4.2 kbar is 297 °K. This fact consists with the pressure at 297 °K as shown in Fig. 6.

3.2 $Cr_7\square Te_8$

The temperature dependence of electrical resistivity for $Cr_7\square Te_8$ (1000 °C) and $Cr_7\square Te_8$ (400 °C) at different hydrostatic pressures are shown in Fig. 8. The Curie temperatures of $Cr_7\square Te_8$ (1000 °C) and $Cr_7\square Te_8$ (400 °C) observed by the electrical resistivity measurements at atmospheric pressure are nearly
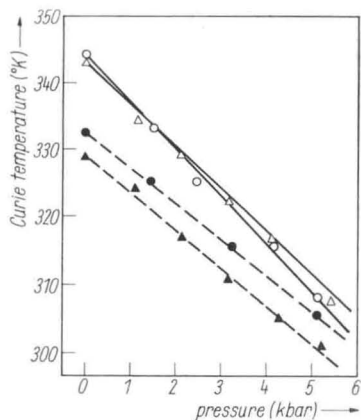

Fig. 9. Pressure dependences of the Curie temperature of $Cr_7\square Te_8$ (1000 °C) (△, ○) and $Cr_7\square Te_8$ (400 °C) (▲, ●). The notations are same as in Fig. 6
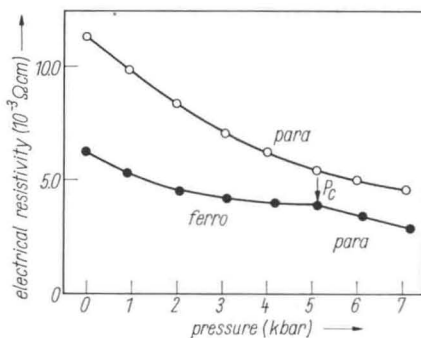
Fig. 10. Pressure dependence of electrical resistivity of $Cr_7\square Te_8$ (1000 °C) in the isotherms at 350 (○) and 308 °K (●)
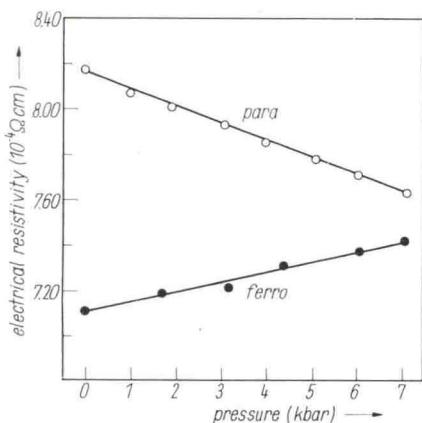
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Fig. 11. Pressure dependence of electrical resistivity of $Cr_7\square Te_8$ (400 °C) in the isotherms at 350 (○) and 290 °K (●)

the same as those previously obtained [3]; there is a difference of about 10 deg between the ordered and disordered phases as shown in Table 1. The pressure shifts in T_C for both phases of $Cr_7\square Te_8$ by the electrical resistivity measurements are shown in Fig. 9 together with those by magnetic induction [3]. The shifting rates for $Cr_7\square Te_8$ are shown in Table 2.

The pressure dependence of ϱ in the isothermal measurements for $Cr_7\square Te_8$ (1000 °C) and $Cr_7\square Te_8$ (400 °C) are shown in Fig. 10 and 11, respectively. The ϱ-value for $Cr_7\square Te_8$ (1000 °C) is about 6×10^{-3} Ωcm at room temperature and atmospheric pressure. Electrical resistivity in the ferromagnetic region decreases with increasing pressure and shows a kink at 5.1 kbar in the isotherm at 308 °K as shown in Fig. 10. This kink is the transition pressure P_C, which corresponds to the pressure at 308 °K in Fig. 9. In case of $Cr_7\square Te_8$ (400 °C) the ϱ-value is approximately 7×10^{-4} Ωcm. As shown in Fig. 11, its electrical resistivity decreases linearly with increasing pressure in the paramagnetic region, but it increases in the ferromagnetic one. The variation of electrical resistivity ϱ in the ferromagnetic region at 290 °K probably will show a kink at about 8 kbar, which corresponds to P_C, because the Curie temperature at 8 kbar seems to be 290 °K in Fig. 9.

In the present study, the results in heating runs were the same as those in cooling runs. These results obtained are shown in Table 1 and 2, where the asterisk indicates the results of the present work, the other are from previous works [2, 3].

4. Discussion

The compounds $Cr_3\square Te_4$ and $Cr_7\square Te_8$ have no thermal hysteresis and no discontinuous change in magnetic induction and electrical resistivity, which exhibit the second-order magnetic transition. The molecular field approximation will be applied to discuss these ferromagnetic compounds. As shown in Table 1, the Curie temperature for $Cr_3\square Te_4$ (1000 °C) is similar to that for $Cr_3\square Te_4$ (cooled slowly). Therefore, it is considered that the magnetic structure of $Cr_3\square Te_4$ (1000 °C) is the same as that of $Cr_3\square Te_4$ (cooled slowly) reported by Andresen [4]. The similar value of T_C can be explained by using the same analysis as in the previous paper [3], since the cell volume at atmosheric pressure is not different in both the phases. The calculated Curie temperature T_C^{cal} for $Cr_3\square Te_4$ (1000 °C) was obtained by the molecular field approximation. A con-

siderable difference was obtained between T_C^{cal} and T_C^{obs} for $Cr_3\square Te_4$ (1000 °C), like in $Cr_3\square Te_4$ (cooled slowly) [2], and in $Cr_7\square Te_8$ [3]. This difference cannot be explained by the volume effect of the exchange interaction. Therefore, we make an assumption in addition to the molecular field approximation for the compound $Cr_{1-\delta}Te$ as follows. If the ionic formula is applied as $\square_\delta Cr_{1-3\delta}^{2+}Cr_{2\delta}^{3+}Te^{2-}$, the exchange interaction between Cr^{2+} and Cr^{3+} ions in accordance with the variation in δ contributes to the enhancement of T_C^{cal} corresponding to the term $(\partial T_C/\partial \delta)_v$. Therefore, the following relation may be proposed:

$$dT_C = \left(\frac{\partial T_C}{\partial V}\right)_\delta \left(\frac{dV}{d\delta}\right) d\delta + \left(\frac{\partial T_C}{\partial \delta}\right)_v d\delta . \tag{1}$$

The value of ΔT_C^{cal} was calculated from the second term, and the estimated Curie temperature T_C^{est} was obtained by adding ΔT_C^{cal} to T_C^{cal} for each compound. As shown in Table 3, the largest value of ΔT_C^{cal} is about 120 °K for $\delta = 0.25$. This implies that T_C^{cal} of $Cr_3\square Te_4$ is largely promoted in comparison with other compounds of $Cr_{1-\delta}Te$ system. However, T_C^{est} ($= 210$ °K) of $Cr_3\square Te_4$ is still different from T_C^{obs} ($= 325$ °K). If the molecular field approximation is applied for the MLD-type compound $Cr_{1-\delta}Te$, it is necessary to consider the interaction between the magnetic atoms in a farther distance, and also the term of volume compressibility.

The electrical resistivity measurements are performed for $Cr_3\square Te_4$ (1000 °C) and $Cr_7\square Te_8$ (1000 °C), (400 °C) in the present work. The values of dT_C/dP from the electrical resistivity measurements consist with those from the magnetic induction method, as tabulated in Table 2. This fact means that electrical resistivity shows a coherent behaviour in proportion to the magnetic properties in $Cr_3\square Te_4$ and $Cr_7\square Te_8$. However, the Curie temperature for $Fe_3\square Se_4$ [5], and $Mn_{1+\delta}Sn$ [7] could not be determined from the electrical resistivity measurements, because of the presence of the fictitious peaks for $Fe_3\square Se_4$ and no anomalous change of ϱ at T_C for $Mn_{1+\delta}Sn$. The difference by an order of magnitude of ϱ-value observed between the two phases of $Cr_7\square Te_8$ at atmospheric pressure is probably caused by the change of MLD ordering.

Table 3

The Curie temperature of $Cr_{1-\delta}Te$ compound calculated from that of CrTe

compound	δ	T_C^{obs} (°K)	T_C^{cal} (°K)	ΔT_C^{cal} (°K)	T_C^{est} (°K)
CrTe	0	350 [6]	—	—	—
$Cr_7\square Te$	0.125	332 [3]	130	50	180
$Cr_5\square Te_6$	0.17	327 [4]	—	60	—
$Cr_3\square Te_4$	0.25	325 [2]	90	120	210
$Cr_2\square Te_3$	0.33	182 [4]	—	40	—

δ: nonstoichiometric parameter in $Cr_{1-\delta}Te$, T_C^{obs}: the observed Curie temperature, T_C^{cal}: the calculated Curie temperature, ΔT_C^{cal}: the shift in T_C calculated from the second term in equation (1), T_C^{est}: the Curie temperature estimated as $T_C^{est} = T_C^{cal} + \Delta T_C^{cal}$.

On the other hand, little difference in dT_C/dP is observed between $Cr_3\square Te_4$ (1000 °C) and $Cr_3\square Te_4$ (cooled slowly) by both the electrical resistivity and magnetic induction measurements. The ϱ values of $Cr_3\square Te_4$ are similar in the two phases at atmospheric pressure. These phenomena observed for $Cr_3\square Te_4$ are also found in $Fe_3\square Se_4$ [5]. It is considered that in $Cr_3\square Te_4$ both the magnetic and electrical properties on the basis of the magnetic transition have little relation to the slight deviation from the ordered sites of MLD, but in $Cr_7\square Te_8$ some relations exist.

In the isothermal measurements of electrical resistivity for the compound $Cr_{1-\delta}Te$ the transition point from the ferromagnetic to the paramagnetic region corresponds to the results shown in Fig. 6 and 9. However, the increase of electrical resistivity ϱ was observed in accordance with the pressure hysteresis. As a cause of this behaviour it may be considered that some lattice imperfections in the crystal are enhanced by pressure and thermal cycles and this phenomenon sensitively influences the scattering of electrons in the conduction mechanism, because the samples used in this work were polycrystalline.

Consequently, the exchange interaction mechanism for the MLD-type compounds, such as $Cr_3\square Te_4$ and $Cr_7\square Te_8$, cannot be explained by a simple molecular field approximation, but should be considered by the effective superexchange pairs through MLD. Moreover, the exchange effect between Cr^{2+} and Cr^{3+} ions corresponding to the variation in δ must be emphasized in the consideration of exchange mechanisms. However, the remarkable difference still remains between T_C^{obs} and T_C^{est}. In order to interpret this difference, a decisive factor must exist in the exchange mechanism. It seems to fit that the MLD itself has a pseudo-atomic nature in the MLD-type compound $Cr_{1-\delta}Te$.

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