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Magnetic and structural properties of pseudo-binary compounds $CrAs_{1-x}P_x$

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Abstract

Structural and magnetic properties of pseudo-binary compounds $\operatorname{CrAs}_{1-x} P_x$ ($0 \le x \le 1$) with the MnP-type structure have been studied by X-ray diffraction, magnetic susceptibility measurements, and differential thermal analysis. For the compounds with x = 0 and 0.03, the lattice parameters *a* and *c* increase abruptly, and *b* and *v* (unit cell volume) decrease abruptly at 265 and 110 K, respectively, which are considered to correspond to the Néel temperature (T_N), as temperature increases. Magnetic susceptibility of all the prepared compounds shows feasible temperature dependence at temperatures from 4.2 to 300 K. The decrease of T_N with *x* is discussed based on the *x* dependence of lattice parameters.

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1. Introduction

Pnictides CrAs and CrP are the compounds with the crystal structure of a MnP-type as shown in Fig. 1. Neutron diffraction studies for CrAs have been done by Kazama and Watanabe [1], Boller and Kallel [2], and Selte et al. [3]. According to their results, CrAs is an antiferromagnet with the Néel temperature (T_N) of 248 K [1], 260 K [2], and 280 K [3], respectively, the magnetic structure of which is a double helical one propagating along the *c*-axis. Magnetic transition at T_N occurs as the first-order transition accompanying the abrupt changes of lattice parameters. However, it is reported that its magnetic susceptibility has feasible temperature dependence at temperatures from 4.2 to 1000 K and does not show any remarkable anomaly at T_N [1,2]. The neutron diffraction study by Selte et al. [4] shows that no magnetic order appears in CrP down to 1.5 K.

There have been reports for magnetic properties of pseudo-binary Cr pnictides with the MnP-type crystal structure: $CrAs_{1-x}P_x$ by Selte et al. [5], $CrAs_{0.98}Sb_{0.02}$ and $Cr_{1-x}M_xAs$ (M = Ti, Fe, Co, Ni) by Suzuki and Ido [6,7], $Cr_{1-x}V_xAs$ by Selte et al. [8], and $CrAs_{1-x}Sb_x$ by Kamigaki et al. [11], Yoshida et al. [10], and Suzuki and Ido [9]. In all the above reports, their magnetic properties

are discussed in the relation with the crystal parameters in order to make clear the origin of their antiferromagnetism. It is reported that the Néel temperature of $CrAs_{0.95}P_{0.05}$ is 246–260 K in [5] and that of $CrAs_{0.98}P_{0.02}$ 150 K in [6], respectively. The effect of the substitution of As by P on the Néel temperature is very different from each other.

In this paper, the structural and magnetic properties of pseudo-binary compounds $CrAs_{1-x}P_x$ are studied in order to make clear the origin of the occurrence of antiferromagnetic order in the 3d transition metal pnictide with the MnP-type crystal structure.

2. Sample preparations and experimental procedures

Samples were prepared in the following ways: powders of Cr (99.9%), As (99.99%), and P (99.99%) were mixed in the desired proportions, sealed in an evacuated silica tube, (1) kept for 3 days after slow heating to $300 \,^{\circ}$ C, (2) for 3 days after slow heating to $600 \,^{\circ}$ C, and (3) for 7 days after slow heating to $800 \,^{\circ}$ C, and then cooled down slowly in the furnace. The products thus obtained were crushed, mixed to homogenize and then pressed into the pellets. The heat-treatments of the pellets were done again following the above three processes and finally heated for 7 days at 900 $\,^{\circ}$ C, and then cooled in the furnace. The 10 samples with *x* = 0, 0.03, 0.05, 0.1, 0.2, 0.3, 0.5, 0.6, and 1 were prepared with

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Fig. 1. Crystal structure of a MnP-type.

the same procedures. The compounds $\operatorname{CrAs}_{1-x}\operatorname{Sb}_x (x = 0.2 \text{ and } 0.3)$ with the MnP-type structure were also prepared in the same way as mentioned above. X-ray diffraction analysis showed that all the prepared samples are in a single phase with the MnP-type crystal structure. The results of chemical analysis showed that the compositions of the prepared samples coincide with the nominal compositions.

Powder X-ray diffraction measurements were carried out at temperatures from 90 to 300 K. Magnetic susceptibility was measured by using a magnetic balance at temperatures from 4.2 to 300 K under magnetic fields from 2 to 11.7 kOe. Differential thermal analysis (DTA) was done by a conventional method.

3. Experimental results

Fig. 2 shows the composition dependence of the lattice parameters *a*, *b*, *c*, and the unit cell volume *v* at room temperature. As seen in the figure, the parameters *a* and *b* are almost constant, but *b* decreases sharply to x = 0.05. In the composition range of x > 0.2, *a*, *b*, and *c* decrease almost linearly with *x*. The results agree well with those by Selte et al. [6]. The unit cell volume *v* also decreases sharply with *x* for x = 0.1 and linearly with *x* for x > 0.1.

Fig. 3 shows the temperature dependence of the unit cell volume v and the lattice parameters a, b, and c for the compounds with x = 0, 0.03, and 0.05. With increase of temperature, a and c increase, and b and v decrease abruptly at 270 K for x = 0, which corresponds to the Néel temperature. The abrupt changes of a, b, and c were also observed



Fig. 2. Composition dependence of a, b, c, and the unit cell volume v.

at 110 K for x = 0.03. The transition temperature of 110 K is considered to be the Néel temperature of $CrAs_{0.97} P_{0.03}$, since the temperature of 270 K mentioned above agrees with the Néel temperature of CrAs. These abrupt changes of the lattice parameters show that the transitions are of the first order. The temperature dependence of the lattice parameters for x = 0.05 does not show any remarkable anomalies in the temperature range of this measurement, which shows that no magnetic order occurs in $CrAs_{0.95}P_{0.05}$ down to 90 K. The temperature dependence of the lattice parameters were



Fig. 3. Temperature dependence of v, a, b, and c for $CrAs_{1-x}P_x$ with x = 0, 0.03, and 0.05.

also measured for $CrAs_{0.8}P_{0.2}$ and $CrAs_{0.6}P_{0.4}$, in which any anomalies were not observed at temperatures from 90 to 300 K.

Table 1 shows the change of the lattice parameters above and below the transition temperature. The change is characterized from that $(c - \sqrt{3}b)/c$ changes its sign from negative value to positive one at the transition temperature as follows: $(c - \sqrt{3}b)/c = -8 \times 10^{-3} (T < T_N)$ and 35×10^{-3} $(T > T_N)$ for CrAs and $-5.7 \times 10^{-3} (T < T_N)$ and 59×10^{-3} $(T > T_N)$ for CrAs_{0.97}P_{0.03}.

Magnetic measurements have been carried out at temperatures from 4.2 to 300 K under magnetic field from 2 to 11.7 kOe by using a magnetic balance. Fig. 4 shows the magnetization curves for the samples with x = 0.03, 0.2, 0.3, 0.4, and 0.6 at 4.2 K, in which all the magnetizations

Table 1

	$\Delta a/a_0$	$\Delta b/b_0$	$\Delta c/c_0$	$\Delta v/v_0$
CrAs CrAs _{0.97} P _{0.03}	$\begin{array}{c} -5.0 \times 10^{-3} \\ -3.5 \times 10^{-3} \end{array}$	$\begin{array}{c} 3.0 \times 10^{-3} \\ 5.6 \times 10^{-3} \end{array}$	$\begin{array}{c} -5.6 \times 10^{-3} \\ -8.8 \times 10^{-3} \end{array}$	1.9×10^{-3} 3.8×10^{-3}

 a_0 , b_0 , and c_0 are the values just above T_N .



Fig. 4. Magnetization curves for $CrAs_{1-x}P_x$ with 0.03, 0.2, 0.3, 0.4, and 0.6 at 4.2 K.



Fig. 5. Temperature dependence of magnetic susceptibilities for $CrAs_{1-x}P_x$ with 0.05, 0.2, 0.3, 0.4, and 0.6.

increase linearly with field. As seen in the figure, magnetic susceptibilities become large with decrease of x from x = 0.6 to 0.2. But it should be noted that the susceptibility for x = 0.03 becomes small again in spite of further decrease of x. Fig. 5 shows the temperature dependence of magnetic susceptibilities of the samples with x from 0.05 to 0.6. The values of susceptibilities increase with decrease of x in this composition range. The susceptibilities for x = 0.4 and 0.6 are almost independent of temperature, but those for x = 0.05, 0.2, and 0.3 increase at low temperatures ascribing to the impurity effect. Fig. 6 shows the temperature dependence



Fig. 6. Temperature dependence of magnetic susceptibilities for $CrAs_{1-x}P_x$ with x = 0, 0.03, 0.05, and 0.6.



Fig. 7. Thermal differential analysis for CrAs.

of susceptibilities for x = 0 and 0.03, together with those for x = 0.05 and 0.6. It is noted that the susceptibilities for x = 0 and 0.03 are smaller than that for 0.05, although the composition became smaller. And then the susceptibilities for x = 0 and 0.03 appear to decrease slightly at lower temperatures, but, the susceptibility peak characteristic of usual antiferromagnet is not observed at T_N .

Differential thermal analysis was carried out for the samples with x = 0 and 0.03 in order to make clear the magnetic transition temperature. As shown in Fig. 7, the result of DTA shows that the transitions occur at 261 K on cooling and 268 K on heating for CrAs, respectively. The transition temperatures on heating almost agree with those of anomalies observed in the temperature dependence of lattice parameters on heating. The result for CrAs_{0.93}P_{0.03} shows that the transitions also occur at 84 K on cooling and 106 K on heating, respectively. The existence of thermal hysteresis observed above indicates that the transitions are of the first order, which correspond the abrupt changes of the lattice parameters at transition.

4. Discussions

In the lattice parameters *a*, *b*, and *c* versus composition *x* curves at room temperature shown in Fig. 2, a_{ext} , b_{ext} , and c_{ext} which are obtained by extrapolating to x = 0, the linear parts of *a*, *b*, and *c*–*x* curves for x > 0.2 are $a_{ext} = 5.66$ Å, $b_{ext} = 3.407$ Å, and $c_{ext} = 6.218$ Å, respectively. The observed lattice parameters for x = 0 are $a_{ob} = 5.66$ Å, $b_{ob} = 3.474$ Å, and $c_{ob} = 6.203$ Å, respectively. And then the values of $(a_{ob} - a_{ext})/a_{ext}$, $(b_{ob} - b_{ext})/b_{ext}$, and $(c_{ob} - c_{ext})/c_{ext}$ are obtained to be -2.6×10^{-3} , 19×10^{-3} , and -2.4×10^{-3} , respectively. The results show that *b* increases rapidly in the

range of low x. On the other hand, the temperature dependence of the lattice parameters for x = 0 and 0.03 show that a and c decrease and b increases with setting of magnetic order below $T_{\rm N}$. The ratio of the changes of b is eight times larger than those of a and c. These results suggest that the rapid increase of b in the range of low x is closely connected to the occurrence of magnetic order. Similar relation between the magnetic order and lattice parameters is observed in $Cr_{1-x}V_xAs$ by Selte et al. [8]. In the case of $Cr_{1-x}V_xAs$, a and c increase with x and their x dependence is opposite to those in $CrAs_{1-x}P_x$, but b decreases at first rapidly with x and has a similar x dependence with that in $CrAs_{1-x}P_x$. Thus, only *b* has the same *x* dependence in both compounds. According to the results by Selte et al., an antiferromagnetic order occurs for x < 0.5 in $Cr_{1-x}V_xAs$. It is considered that the occurrence of antiferromagnetism in those Cr compounds with the MnP-type structure has a close relation with the rapid increase of b from the results mentioned above, since the *a* lattice parameters at room temperature are the values in a paramagnetic state free from the large exchange striction occurring in the antiferromagnetic state.

As shown in Fig. 6, the temperature dependence of magnetic susceptibilities of CrAs, CrAs_{0.97}P_{0.03}, CrAs_{0.8}Sb_{0.2}, and CrAs_{0.7}Sb_{0.3} compounds are characterized by the slight increase of susceptibility on heating through T_N and the absence of susceptibility peaks at T_N . It is known that the crystal structure of both pseudo-binary compounds changes into the NiAs-type structure from the MnP-type one at high temperatures, in which the distance between Cr atoms become larger. It is considered that the increase of susceptibility on heating is ascribed to the approach to the NiAs-type structure with larger unit cell volume. On the other hand, it is well known that the susceptibility peak does not appear at $T_{\rm N}$ in an itinerant electron antiferromagnet Cr being a spin density wave. Lack of susceptibility peak at T_N for CrAs and CrAs_{0.97}P_{0.03} in Fig. 8 is considered their magnetic property to be ascribed to itinerant electron magnetism.

Selte et al. have reported that the Néel temperature of CrAs_{0.95}P_{0.05} is 246–260 K, a little lower than that of CrAs. In the present study, however, any anomaly corresponding to $T_{\rm N}$ was not observed in the temperature dependence of lattice parameters at temperatures from 100 to 300 K for $CrAs_{0.95}P_{0.05}$. On the other hand, anomalies were observed at 110 K in the thermal expansions of lattice parameters and at 104 K in DTA, respectively, for CrAs_{0.97}P_{0.03}. Fig. 9 shows the Néel temperatures for $CrAs_{1-x}P_x$ with x = 0.02, 0.03, and 0.05 by Suzuki and Ido [6], the present study, and Selte et al. [5], respectively. As shown in the figure, the Néel temperatures for x = 0, 0.02, and 0.03 are almost on a straight line, in which T_N appears to become 0 around $x \sim 0.05$. There is a large discrepancy between the effects of substitution of As with P on T_N by Selte et al. and the above results. Once, Suzuki and Ido [6] have pointed out that the appearance of antiferromagnetism in Cr pnictides with the MnP-type structure connects strongly with the value of b and there exists a critical b value of $b_c = 3.38$ Å, below

Fig. 8. Temperature dependence of magnetic susceptibilities for $CrAs_{1-x}P_x$ with x = 0 and 0.03 and $CrAs_{1-x}Sb_x$ with x = 0.2 and 0.3.

which no magnetic order occurs. As mentioned above, b_c for the CrAs_{1-x}P_x compounds is ~3.42 Å corresponding to $x \sim 0.05$; and then b_c for Cr_{1-x}V_xAs is also estimated to be ~3.43 Å [8].

As described above, the substitution of As with P decreases the unit cell volume v of the compounds. The Néel temperature of $CrAs_{0.97}P_{0.03}$ can be estimated using the pressure dependence of T_N of CrAs, if the decrease of T_N with P addition can be assumed to be only due to the de-



0.04

х

0.06

0.02

0

0





crease of v. The decrease ratio of v of CrAs_{0.97}P_{0.03} to CrAs is $(v_{x=0.03} - v_{x=0})/v_{x=0} = -0.013$. At present, there is no report on a volume compressibility of CrAs. Thus, the pressure necessary to decrease v by -1.3% is estimated to be about 10 kbar if we use the compressibility $k = 1.34 \times 10^{-3}$ per kbar. And the pressure change of T_N for CrAs is $dT_N/dp = -12$ K/kbar [10] and -15 K/kbar [12], respectively. From these results, T_N of CrAs_{0.97}P_{0.03} is estimated to be 120–150 K, which is a little higher than the observed value.

It is desirable that the relation between the occurrence of magnetic order and the crystallographic parameters will be clarified experimentally by the measurements of pressure change of the lattice parameters, especially of *b*, in CrAs by X-ray diffraction under pressure.

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References

- [1] N. Kazama, H. Watanabe, J. Phys. Soc. Japan 30 (1971) 1319.
- [2] H. Boller, A. Kallel, Solid State Commun. 9 (1971) 1666.
- [3] K. Selte, A. Kjekshus, W.E. Jamison, A.F. Andressen, J.E. Engebretsen, Acta Chem. Scand. 25 (1971) 1703.
- [4] K. Selte, A. Kjekshus, A.F. Andressen, Acta Chem. Scand. 26 (1972) 4188.
- [5] K. Selte, H. Hjersing, A. Kjekshus, A.F. Andressen, P. Fisher, Acta Chem. Scand. A29 (1975) 695.
- [6] T. Suzuki, H. Ido, J. Appl. Phys. 73 (1993) 5688.
- [7] T. Suzuki, H. Ido, J. Appl. Phys. 69 (1991) 4624.
- [8] K. Selte, H. Hjersing, A. Kjekshus, A.F. Andressen, Acta Chem. Scand. A29 (1975) 312.
- [9] A. Kallel, H. Boller, E.F. Bertaut, J. Phys. Chem. Solids 35 (1974) 1139.
- [10] H. Yoshida, T. Kaneko, M. Shono, S. Abe, M. Ohashi, J. Magn. Magn. Mater. 15–18 (1980) 1147.
- [11] K. Kamigaki, M. Shono, H. Yoshida, S. Abe, T. Kaneko, J. Magn. Magn. Mater. 70 (1987) 218.
- [12] E.A. Zavadskii, I.A. Sibarova, Sov. Phys. Solid State 18 (1976) 1009.