

Phase Diagram of $(M'_x M_{1-x})_3 \text{Se}_4$ ($0 \leq x \leq 1$) (M, M' = 3d-transition metal)

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The phase diagram of $(M'_x M_{1-x})_3 \text{Se}_4$ ($0 \leq x \leq 1$; M, M' = 3d-transition metal) was determined by DTA and high-temperature X-ray diffraction. The obtained phase diagrams were classified into two groups: (a) solid solution type; (b) phase separation type. In the (a) group, the phase transition from the Cr_3S_4 - to CdI_2 -structure was observed over a whole composition range in each system. In the (b) group, a solid solution with the CdI_2 -structure was also observed at higher temperature. Some features of the phase diagram were discussed from the viewpoint of the cation distribution in these systems.

KEY WORDS: Phase diagram/ Transition metal chalcogenide/ Order-disorder transition/

INTRODUCTION

The 3d-transition metal chalcogenides, $M_{1+y}X_2$ (M: 3d-transition metal, X: chalcogen, $0 \leq y \leq 1$), are of interest with respect not only to their various physical properties but also to the phase relation and structural aspect. A number of vacancy-ordered phases with the characteristic structures based on the NiAs - or CdI_2 -structure, M_5X_8 , M_2X_3 , M_3X_4 , M_7X_8 etc., appear in the composition range $0 \leq y$

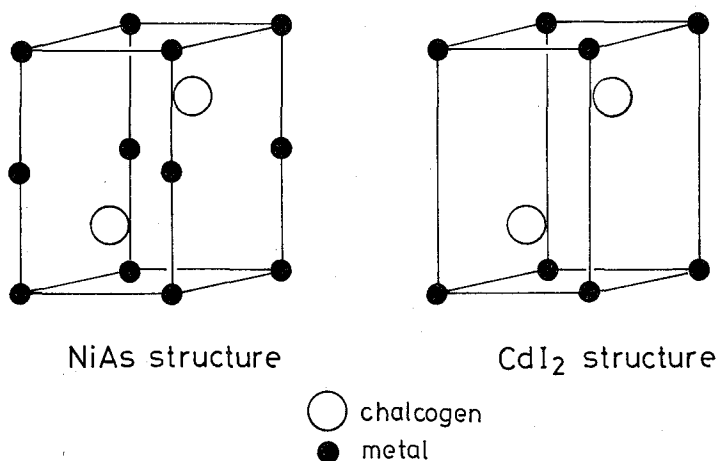


Fig. 1. Schematic drawing of the NiAs - and CdI_2 -structure

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≤ 1 . These structures are easily understood by the following general principle. Metal atoms occupy octahedral holes of hexagonally close-packed chalcogen atoms. One end member MX with the NiAs-structure has only fully-occupied metal layers, while the other end member MX_2 with the CdI_2 -structure has the alternate stacking of fully-occupied and unoccupied metal layers (see Fig. 1). In the intermediate composition $M_{1+y}X_2$ ($0 < y < 1$), the unoccupied layers (van der Waals' gap) in the CdI_2 -structure are partially occupied by the excess metal atoms y . Therefore, the layer stacking is generally $M^fXM^vXM^fX\cdots$, where M^f denotes the metal layer fully occupied and M^v the metal layer partially occupied. Moreover, metal-vacancies are characteristically arranged both within M^v layers and along the direction perpendicular to the layers at the specific composition.

Among these metal-vacancy-ordered phases, M_3X_4 phase with the Cr_3S_4 -structure* (monoclinic) appears in many $M_{1+y}X_2$ systems. Since this structure was first reported by Okazaki and Hirakawa in 1956,¹⁾ a number of isostructural compounds have been reported. The electric and magnetic properties of the compounds with the Cr_3S_4 -structure are summarized in Table I. In the Cr_3S_4 -structure, M^v layers are just half occupied and the metal-vacancies are arranged in such a manner as shown in Fig. 2. There exist two kinds of sites for metal atoms in this structure; the site I in M^v layers and the site II in M^f layers in the ratio 1:2.

On the basis of such a structural feature, many isostructural ternary compounds with the general formula $M'M_2X_4$ have been also synthesized. Table II shows these compounds with their electric and magnetic properties. In these compounds, a metal-ordered structure is of interest. The type of the metal-ordered structure was first reported by Chevreton and Andron.²⁾ They proposed the two cases on

Table I. Compounds with the Cr_3S_4 -structure

Compound	Electric property ^{a)}	Magnetic property ^{b)}	References
V_3S_4	M	AF	12, 26, 41-47
Cr_3S_4	M	AF	12, 42, 48-51
Ti_3Se_4	M	PP	52
V_3Se_4	M	AF	26, 45, 52-56
Cr_3Se_4	SC	AF	27, 49, 50, 57-60, 100, 101, 104
Fe_3Se_4	SC	Fr	1, 61-64, 102, 103
Co_3Se_4	—	PP	15, 65, 66
Ni_3Se_4 ^{c)}	—	PP	32-34
Ti_3Te_4	—	PP	19, 30, 52
V_3Te_4	M	P	20, 28, 67-70
Cr_3Te_4	—	F(+AF)	19, 20, 49, 50, 60, 71-75, 99, 104

a) M: metallic, SC: semiconductive

b) P: paramagnetic, PP: Pauli paramagnetic, AF: antiferromagnetic, F: ferromagnetic, Fr: ferrimagnetic

c) The mixture with $NiSe_2$.

* This structure is usually called as " Cr_3S_4 -structure" in spite of the first proposal for Fe_3Se_4 .

Table II. $M'M_2X_4$ with the Cr_3S_4 -structure

(a) Sulfides

Compound	Electric property ^{a)}	Magnetic property ^{b)}	References
FeTi ₂ S ₄	M	AF + F, F	38, 39, 76–83, 105
CoTi ₂ S ₄	M	PP	38–40, 81, 105
NiTi ₂ S ₄	M	PP	38–40, 81, 105
CrV ₂ S ₄	M, SC	AF	11, 12, 42
FeV ₂ S ₄	M	AF	7–9, 40, 41, 79, 84, 85, 97
CoV ₂ S ₄	M	PP	40, 41, 85
NiV ₂ S ₄	M	PP	40, 41, 85, 86
TiCr ₂ S ₄	M	AF	5, 41, 42
VCr ₂ S ₄	SC	AF	10, 42
FeCr ₂ S ₄ ^{c)}	—	AF	87
CoCr ₂ S ₄ ^{c)}	—	AF	87
NiCr ₂ S ₄	SC	AF + F	4, 35, 42, 48, 86, 87
TiFe ₂ S ₄	SC	Fr	88
VFe ₂ S ₄	—	AF	7, 9

(b) Selenides

Compound	Electric property ^{a)}	Magnetic property ^{b)}	References
VTi ₂ Se ₄	—	—	37
CrTi ₂ Se ₄	—	—	30, 89
FeTi ₂ Se ₄	M	AF	37–40, 79, 84
CoTi ₂ Se ₄	M	PP	37–40
NiTi ₂ Se ₄	M	PP	37–40
CrV ₂ Se ₄	—	—	37
FeV ₂ Se ₄	M	AF	37, 40, 79, 84, 90
CoV ₂ Se ₄	—	PP	37, 40
NiV ₂ Se ₄	M	PP	37, 40, 86, 91
TiCr ₂ Se ₄	—	F	5, 30, 36
VCr ₂ Se ₄	—	—	36
FeCr ₂ Se ₄	SC	AF	2, 6, 16, 35, 36, 92, 96
CoCr ₂ Se ₄	SC	AF	35, 36
NiCr ₂ Se ₄	SC	AF	35, 36, 86
TiFe ₂ Se ₄	SC	Fr	37, 93, 94
VFe ₂ Se ₄	M	Fr	37, 93
CrFe ₂ Se ₄	SC	Fr	16, 37, 93, 94
CoFe ₂ Se ₄	M	Fr	15, 37, 93, 94
NiFe ₂ Se ₄	M	Fr	15, 37, 93, 94
VCo ₂ Se ₄	—	—	37
FeCo ₂ Se ₄	—	P	15, 37
NiCo ₂ Se ₄	—	—	37
FeNi ₂ Se ₄	—	P	15, 37
CoNi ₂ Se ₄	—	—	37

(c) Tellurides

Compound	Electric property ^{a)}	Magnetic property ^{b)}	References
VTi ₂ Te ₄	—	—	95
CrTi ₂ Te ₄	—	F	19, 30, 95
TiV ₂ Te ₄	—	—	95
CrV ₂ Te ₄	—	F	20, 95
FeV ₂ Te ₄	M	AF	98
TiCr ₂ Te ₄	—	F	3, 19, 95
VCr ₂ Te ₄	—	F	20, 95

a) M: metallic, SC: semiconductive

b) AF: antiferromagnetic, F: ferromagnetic, Fr: ferrimagnetic, PP: Pauli paramagnetic

c) Synthesized under high pressure.

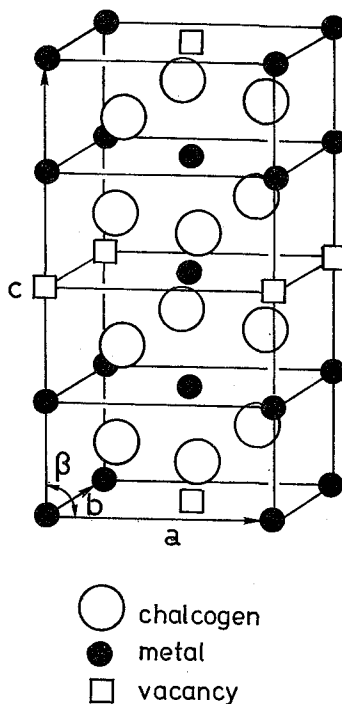


Fig. 2. Unit cell of the Cr₃S₄-structure

the analogy of those for the spinel compounds; (1) normal-type $(M')[MM]X_4$, (2) inverse-type $(M)[M'M]X_4$, where parentheses and brackets denote M^v and M^f layers, respectively. In fact, such metal-ordered structures have been found in several compounds mainly by neutron diffraction.²⁻⁷⁾

In addition to these binary or ternary compounds, some pseudo-binary systems M_3X_4 - M'_3X_4 have also been studied mainly with a view to the electric and magnetic properties. The systems reported are as follows. (a) Sulfide system: V_3S_4 -

FeV_2S_4 ,⁸⁾ V_3S_4 — VFe_2S_4 ,⁹⁾ Cr_3S_4 — V_3S_4 ¹⁰⁻¹²⁾ and V_3S_4 — Ti_3S_4 .^{13,14)} (b) Selenide system: Ni_3Se_4 — Fe_3Se_4 ,¹⁵⁾ Co_3Se_4 — Fe_3Se_4 ,¹⁵⁾ and Cr_3Se_4 — Fe_3Se_4 .¹⁶⁾ (c) Telluride system: Cr_3Te_4 — Rh_3Te_4 ,^{17,18)} Cr_3Te_4 — Ti_3Te_4 ,¹⁹⁾ and Cr_3Te_4 — V_3Te_4 .²⁰⁾

A study of the site preference of two kinds of metal ions in the pseudo-binary system M_3X_4 — $\text{M}'_3\text{X}_4$ was for the first time made on the solid solution system V_3S_4 — VFe_2S_4 .²¹⁾ As a result, it was confirmed by neutron diffraction,⁷⁾ Mössbauer spectroscopy,²²⁾ Raman spectroscopy²³⁾ and X-ray diffraction²⁴⁾ that Fe ions have a tendency for the site I in the Cr_3S_4 -structure; Fe ions are preferentially substituted for V ions in the site I, starting from V_3S_4 . The site preference of each metal ions was also observed in the system $\text{TiS}_{1.40}$ — $\text{VS}_{1.40}$.^{*13)} Results of the magnetic susceptibility and ^{51}V NMR were successfully interpreted from the model that Ti ions preferentially occupy the site II. Nozaki also discussed the site preference in the Fe-V-S and Ti-V-S systems in relation to the interaction between cations along c-axis.²⁵⁾

Another significant feature of M_3X_4 phase is in the order-disorder transition of the metal-vacancies at higher temperatures. The following three transitions are possible, (1) the transition into the nonstoichiometric CdI_2 -structure (intra-layer disordering of metal-vacancies), (2) the transition into the nonstoichiometric NiAs-structure (intra- and inter-layer disordering) and (3) the successive transition (Cr_3S_4 → CdI_2 → NiAs-structure). Oka *et al.* reported the transition of the type (1) in V_3S_4 and V_3Se_4 .²⁶⁾ The similar transition in Cr_3Se_4 and V_3Te_4 was reported by Ohtani *et al.*.^{27,28)} Wada reported the transition of the type (3) in $\text{Fe}_{0.60}\text{V}_{0.40}\text{S}_x$ ($1.22 < x < 1.35$).²⁹⁾ The phase diagram of the system M_3X_4 — $\text{M}'_3\text{X}_4$ in relation to the order-disorder transition of the metal-vacancies has been scarcely reported. We reported the phase diagram of $(\text{Cr}_x\text{Ti}_{1-x})_3\text{Se}_4$,³⁰⁾ where the lattice parameters and the order-disorder transition temperature (T_c) vs. composition curves were found to show an anomaly at the composition $x=1/3$ (CrTi_2Se_4). We interpreted the behavior from a viewpoint of the selective substitution of Cr ions for Ti ions in the site I and inferred the metal-ordered structure of CrTi_2Se_4 and TiCr_2Se_4 to be the normal- and inverse-type, respectively. Afterward, these metal-ordered structures were confirmed from the cation distribution in CrTi_2Se_4 and TiCr_2Se_4 determined by neutron diffraction.³¹⁾

Selenide systems are suitable in consideration of the site preference of each ion, because all of M_3Se_4 (M: 3d-transition metal) except for $\text{M}=\text{Mn}$ have the Cr_3S_4 -structure. The establishment of the phase diagram of M_3Se_4 — $\text{M}'_3\text{Se}_4$ system is indispensable also to understand their physical properties. In this paper, we report the phase diagrams of $(\text{M}'_x\text{M}_{1-x})_3\text{Se}_4$ with all possible combinations (15 systems**).

EXPERIMENTAL

The samples were prepared by direct reaction of the high-purity elements.

* $\text{TiS}_{1.40}$ has $4\text{H-Ti}_2\text{S}_3$ -type structure.

** We excluded the $(\text{Fe}_x\text{Ti}_{1-x})_3\text{Se}_4$ system because of some complexity. The phase diagram of the $(\text{Fe}_x\text{Ti}_{1-x})_3\text{Se}_4$ system will be discussed in another paper.

Ti (3N), V (2N5), Cr (3N), Co (4N) and Ni (4N) were supplied in powder form. Fe powder was obtained from Fe_2O_3 (4N) by reduction in H_2 . Granular Se (5N) was ground into powder before use. They were mixed in the appropriate ratio, pressed into a disk at 10 kg/cm^2 and sealed in an evacuated silica tube. The tube was then gradually heated up to $800\text{--}900^\circ\text{C}$ and cooled to room temperature in an electric furnace. The products were pulverized and again pressed into a disk, followed by annealing at desired temperatures ($300\text{--}900^\circ\text{C}$) and quenched in ice water. The annealing period was 1 week–1 month. The phase identification of the samples was made with an X-ray diffractometer with monochromatic $\text{Cu K}\alpha$ radiation. The lattice parameters were determined by the least-squares method using the high-angle reflections.

X-ray diffraction patterns at high temperatures were taken with the X-ray diffractometer mounted with the furnace specially designed. The samples were sealed in an evacuated quartz capillary of 1–2 mm in diameter and 0.01 mm thick. To obtain sufficient diffraction intensity, three or four capillaries were mounted on a Pt plate.

Differential thermal analysis (DTA) was carried out in the temperature range from room temperature up to 1100°C . A heating or cooling rate was $20\text{--}50^\circ\text{C/min}$. The samples were sealed under vacuum in a cylindrical silica capsule with the thin-walled bottom (5 mm in diameter and 10 mm in height). Al_2O_3 , Cr powder or blank capsule was used as references.

Electron diffraction patterns and lattice images were obtained with a JEM 100CX electron microscope.

RESULTS AND DISCUSSION

1. Phase relation at room temperature

The samples quenched in ice water after annealing at various temperatures were identified at room temperature by X-ray powder diffraction. The results are as follows.

(a) The systems which form a solid solution with the Cr_3S_4 -structure over a whole composition range;

$(\text{V}_x\text{Ti}_{1-x})_3\text{Se}_4$, $(\text{Cr}_x\text{Ti}_{1-x})_3\text{Se}_4$, $(\text{Cr}_x\text{V}_{1-x})_3\text{Se}_4$, $(\text{Fe}_x\text{V}_{1-x})_3\text{Se}_4$, $(\text{Co}_x\text{V}_{1-x})_3\text{Se}_4$, $(\text{Fe}_x\text{Cr}_{1-x})_3\text{Se}_4$, $(\text{Co}_x\text{Fe}_{1-x})_3\text{Se}_4$, $(\text{Ni}_x\text{Fe}_{1-x})_3\text{Se}_4^*$ and $(\text{Ni}_x\text{Co}_{1-x})_3\text{Se}_4^*$

(b) The systems in which two-phase mixture appeared;

$(\text{Co}_x\text{Ti}_{1-x})_3\text{Se}_4$, $(\text{Ni}_x\text{Ti}_{1-x})_3\text{Se}_4^*$, $(\text{Ni}_x\text{V}_{1-x})_3\text{Se}_4^*$, $(\text{Co}_x\text{Cr}_{1-x})_3\text{Se}_4$ and $(\text{Ni}_x\text{Cr}_{1-x})_3\text{Se}_4^*$

2. DTA

In all systems of the (a) group, one endothermic peak was observed in DTA. The peak temperature smoothly varies with the composition in these systems. Those

* The stoichiometric Ni_3Se_4 was the two-phase mixture of M_3X_4 phase with the Cr_3S_4 -structure and NiSe_2 with the pyrite structure. This result agrees with the previous report on Ni-Se system.^{32–34} Moreover, the pyrite phase appeared near Ni_3Se_4 in the systems $\text{M}_3\text{Se}_4\text{--Ni}_3\text{Se}_4$. However, we omit the pyrite phase in the phase diagram shown later, because of a small amount of the phase.

of V_3Se_4 and Cr_3Se_4 are in good agreement with the order-disorder transition temperature (T_t) reported by Oka *et al.*²⁶⁾ and by Ohtani *et al.*²⁷⁾ At higher temperatures, some samples showed several large endothermic peaks which probably correspond to an appearance of a liquid phase.

In the (b) group, the results of DTA were somewhat complex compared with those in the (a) group. In the solid solution region, one peak similar to that of the (a) group was observed, but two or three thermal anomalies were detected in the two phase region. As an example, the result of DTA in the $(Co_xCr_{1-x})_3Se_4$ system is shown in Fig. 3. The result in the $(Ni_xCr_{1-x})_3Se_4$ system was the similar one, but the DTA curves in the $(Co_xTi_{1-x})_3Se_4$ and $(Ni_xV_{1-x})_3Se_4$ systems did not show such definite peaks as those in the former two systems. In the $(Ni_xTi_{1-x})_3Se_4$ system, no appreciable peak was observed except the endothermic peak at melting points (900–1000°C). In the present study, as is our interest focused mainly on the solid phase relation including the order-disorder transition, no further investigation about the liquid phase was performed.

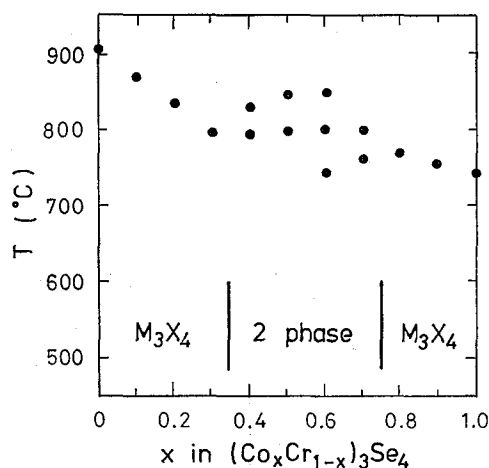


Fig. 3. Transition temperature detected by DTA in the $(Co_xCr_{1-x})_3Se_4$ system

3. High-temperature X-ray diffraction

As is often the case with the transition metal chalcogenide,^{26,27,29)} the high-temperature phases can be hardly quenched to room temperature. Therefore, the high-temperature X-ray diffraction experiments were carried out in several typical samples to clarify the high-temperature phase *in situ*.

3.1 Ni_3Se_4

As mentioned before, nominal " Ni_3Se_4 " was M_3X_4 phase with the Cr_3S_4 -structure including a trace of $NiSe_2$ with the pyrite structure. " Ni_3Se_4 " shows an endothermic peak in DTA at 370°C. Figure 4 shows the temperature dependence of a part of X-ray diffraction patterns characteristic of M_3X_4 phase. The group of peaks at 300°C (M_3X_4 phase) is gathering into a single peak on heating and finally

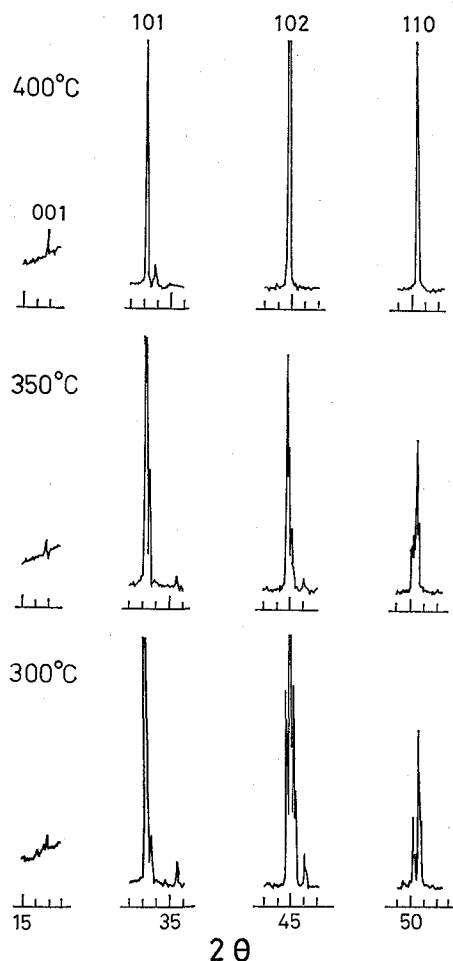


Fig. 4. A part of X-ray diffraction patterns of "Ni₃Se₄" observed at 300, 350 and 400°C. The indices hkl shown in the top of the figure are indexed on the CdI₂-structure.

at 400°C the diffraction patterns completely show those of the CdI₂-structure. The NiAs-structure as another possible high-temperature phase was excluded by the presence of 001 reflection at about $2\theta = 17^\circ$. Consequently, the transition at 370°C was confirmed to be the order-disorder transition from the Cr₃S₄- to CdI₂-structure.

The high-temperature X-ray diffraction of Co₃Se₄ also showed that the transition at 740°C accompanied with an endothermic peak is one from the Cr₃S₄- to CdI₂-structure.

3.2 (Co_{0.6}Cr_{0.4})₃Se₄

As shown in Fig. 3, (Co_{0.6}Cr_{0.4})₃Se₄ showed three endothermic peaks at 740, 800 and 850°C. The X-ray powder diffraction patterns of the sample show those of the mixture of two M₃X₄ phases (Cr- and Co-rich M₃X₄ phase) at room temperature. The results of the high-temperature X-ray diffraction patterns were

those of the mixture of two M_3X_4 phases at 700°C, M_3X_4 phase (Co-rich phase) and CdI_2 phase (Cr-rich phase) at 775°C, two CdI_2 phases at 820°C, and the single phase with the CdI_2 -structure at 900°C. This reveals that two M_3X_4 phases with the Cr_3S_4 -structure separately exhibit the order-disorder transition at different temperature and form a solid solution with the CdI_2 -structure at higher temperature. As seen in Fig. 3, T_t of each phase varies with composition x in the two phase region. The lattice parameters of each phase also varied in this region. This indicates that the tie-lines connecting the coexisting phases cross the binary line Cr_3Se_4 — Co_3Se_4 , because Cr_3Se_4 and Co_3Se_4 phases have the wide nonstoichiometric region.

The similar successive phase transitions were also observed in the $(Ni_xCr_{1-x})_3Se_4$ system.

4. Phase diagram

From the results described in the preceding sections, we obtained following phase diagrams of the $(M'_xM_{1-x})_3Se_4$ systems. The liquidus lines are omitted in the phase diagram shown below.

4.1 $(Cr_xTi_{1-x})_3Se_4$

Figure 5 shows the phase diagram of the $(Cr_xTi_{1-x})_3Se_4$ system.³⁰⁾ The T_t vs. x curve shows a minimum around $x=1/3$ ($CrTi_2Se_4$).

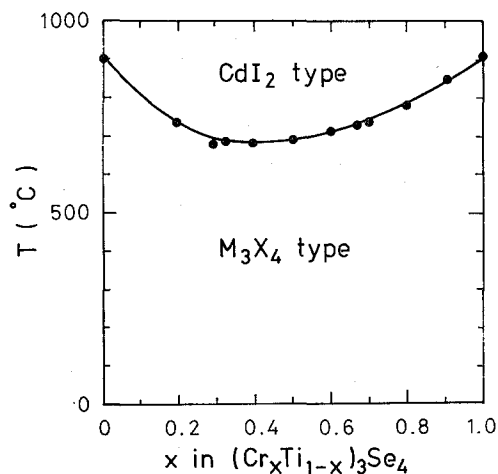


Fig. 5. Phase diagram of the $(Cr_xTi_{1-x})_3Se_4$ system (from Ref. 30)

4.2 $(Cr_xV_{1-x})_3Se_4$

This system also forms a solid solution with the Cr_3S_4 -structure and exhibits the phase transition to the CdI_2 -structure over a whole composition range. As shown in Fig. 6, T_t decreases monotonously as x increases, with slight downward curvature.

Phase Diagram of $(M'_xM_{1-x})_3\text{Se}_4$ ($0 \leq x \leq 1$); ($M, M' = 3d\text{-transition metal}$)

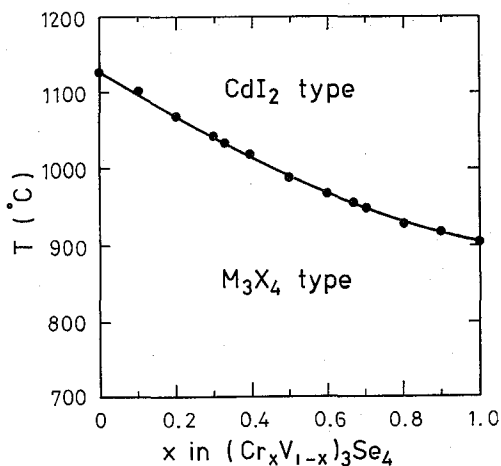


Fig. 6. Phase diagram of the $(\text{Cr}_x\text{V}_{1-x})_3\text{Se}_4$ system

4.3 $(\text{V}_x\text{Ti}_{1-x})_3\text{Se}_4$

The phase diagram of the $(\text{V}_x\text{Ti}_{1-x})_3\text{Se}_4$ system is shown in Fig. 7. The T_t curve changes its curvature around $x=2/3$ (TiV_2Se_4).

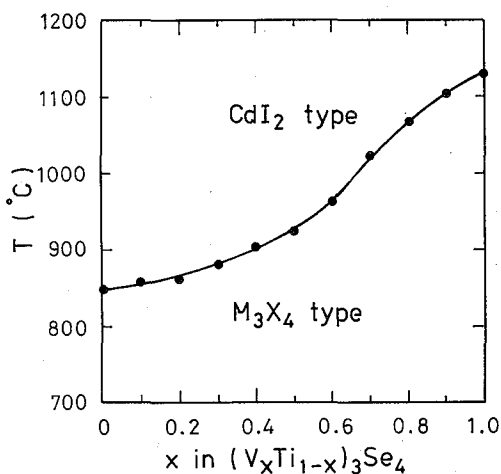


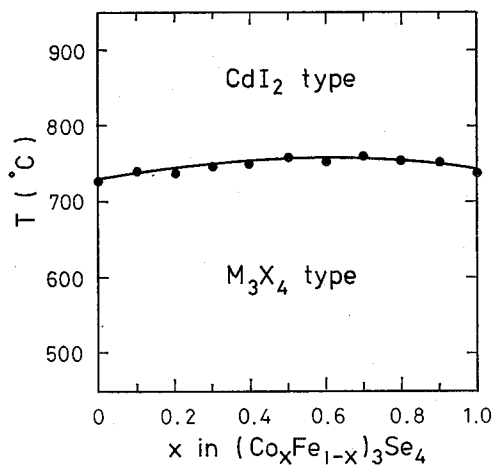
Fig. 7. Phase diagram of the $(\text{V}_x\text{Ti}_{1-x})_3\text{Se}_4$ system

4.4 $(\text{Co}_x\text{Fe}_{1-x})_3\text{Se}_4$

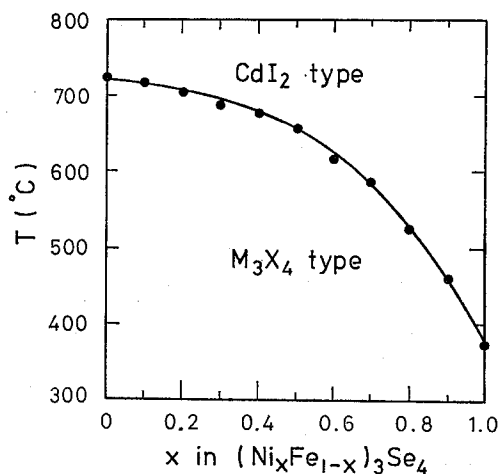
As shown in Fig. 8, this system forms a solid solution over a whole composition range, which agrees with the previous report.¹⁵⁾ The T_t curve shows slight upward curvature.

4.5 $(\text{Ni}_x\text{Fe}_{1-x})_3\text{Se}_4$

As mentioned before, when the samples were quenched from 500°C , a trace of the pyrite phase coexisted with M_3X_4 phase in the composition range of $0.8 \leq x$

Fig. 8. Phase diagram of the $(\text{Co}_x\text{Fe}_{1-x})_3\text{Se}_4$ system

≤ 1.0 . This is consistent with the result reported by Kojima *et al.*¹⁵⁾ However, we treat this system as a solid solution type. Figure 9 shows the phase diagram of the $(\text{Ni}_x\text{Fe}_{1-x})_3\text{Se}_4$ system. T_t decreases with x and its curve shows upward curvature with no anomaly.

Fig. 9. Phase diagram of the $(\text{Ni}_x\text{Fe}_{1-x})_3\text{Se}_4$ system

4.6 $(\text{Ni}_x\text{Co}_{1-x})_3\text{Se}_4$

The pyrite phase also appears in this system. When the samples were quenched from 300°C, the two phase region (M_3X_4 phase + pyrite phase) was in the composition range of $0.2 \leq x \leq 1.0$. As an annealing temperature was raised, the two phase region became narrower ($0.8 \leq x \leq 1.0$ for the samples quenched from 800°C). However, we treat this system as a solid solution type because of small amount of the

Phase Diagram of $(M'_xM_{1-x})_3\text{Se}_4$ ($0 \leq x \leq 1$); ($M, M' = 3d\text{-transition metal}$)

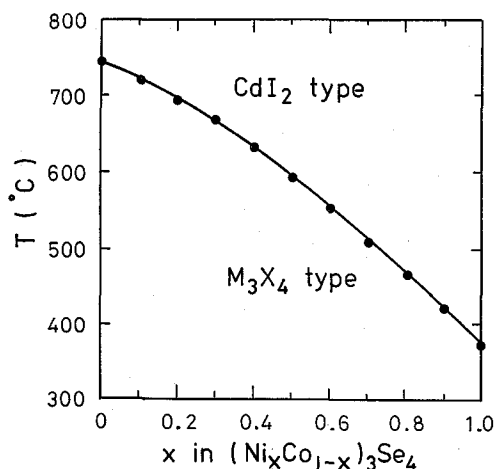


Fig. 10. Phase diagram of the $(\text{Ni}_x\text{Co}_{1-x})_3\text{Se}_4$ system

pyrite phase. Figure 10 shows the phase diagram of the $(\text{Ni}_x\text{Co}_{1-x})_3\text{Se}_4$ system. T_t smoothly decreases as x increases with slight upward curvature.

4.7 $(\text{Fe}_x\text{V}_{1-x})_3\text{Se}_4$

Figure 11 shows the phase diagram of the $(\text{Fe}_x\text{V}_{1-x})_3\text{Se}_4$ system. This system forms a solid solution over a whole composition range and T_t decreases monotonously with x . The T_t curve shows slight downward curvature.

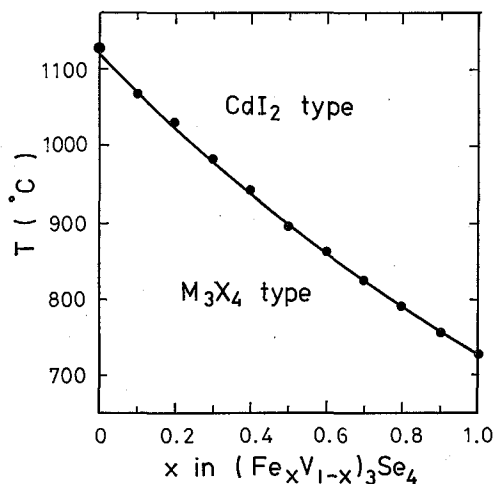
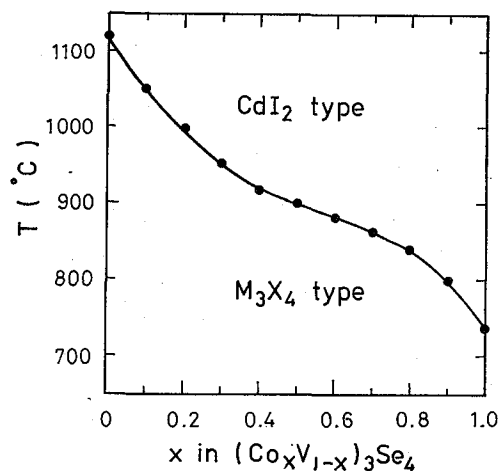


Fig. 11. Phase diagram of the $(\text{Fe}_x\text{V}_{1-x})_3\text{Se}_4$ system

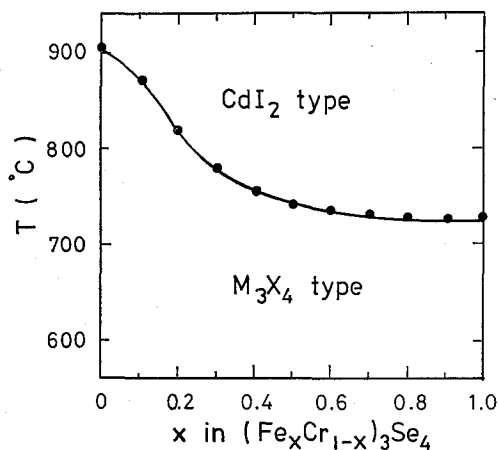
4.8 $(\text{Co}_x\text{V}_{1-x})_3\text{Se}_4$

The phase diagram of the $(\text{Co}_x\text{V}_{1-x})_3\text{Se}_4$ system is shown in Fig. 12. T_t decreases with x and the T_t curve shows a hump around $x=2/3$ (VCo_2Se_4).

Fig. 12. Phase diagram of the $(\text{Co}_x\text{V}_{1-x})_3\text{Se}_4$ system

4.9 $(\text{Fe}_x\text{Cr}_{1-x})_3\text{Se}_4$

This system forms a solid solution with the Cr_3S_4 -structure over a whole composition range as shown in Fig. 13, which is in agreement with the previous report.¹⁶⁾ T_t decreases steeply up to the composition about $x=1/3$ (FeCr_2Se_4), then decreases slightly toward $x=1.0$.

Fig. 13. Phase diagram of the $(\text{Fe}_x\text{Cr}_{1-x})_3\text{Se}_4$ system

4.10 $(\text{Co}_x\text{Cr}_{1-x})_3\text{Se}_4$

This system shows the phase separation as shown in Fig. 14. At low temperature, two phase region of Cr- and Co-rich M_3X_4 phases was in $0.3 \leq x \leq 0.8$. As clarified by the high-temperature X-ray diffraction, each phase transformed into CdI_2 phase at different temperatures. Then at higher temperature, a solid solution with the CdI_2 -structure was formed in $0 \leq x \leq 1$. It is to be noted that " CoCr_2Se_4 " was the two phase mixture in this study, whereas the compound CoCr_2Se_4 with

Phase Diagram of $(M'_xM_{1-x})_3\text{Se}_4$ ($0 \leq x \leq 1$); ($M, M' = 3d\text{-transition metal}$)

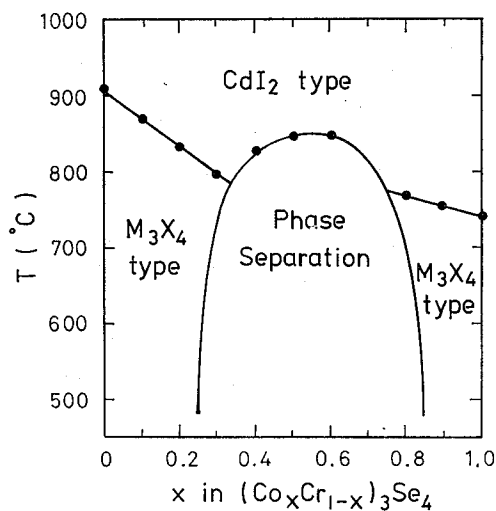


Fig. 14. Phase diagram of the $(\text{Co}_x\text{Cr}_{1-x})_3\text{Se}_4$ system

the Cr_3S_4 -structure was reported.³⁵⁾ Chevreton reported that “ CoCr_2Se_4 ” was not a single phase.³⁶⁾

4.11 $(\text{Ni}_x\text{Cr}_{1-x})_3\text{Se}_4$

Figure 15 shows the phase diagram of the $(\text{Ni}_x\text{Cr}_{1-x})_3\text{Se}_4$ system. The obtained phase diagram is similar to that of the $(\text{Co}_x\text{Cr}_{1-x})_3\text{Se}_4$ system.

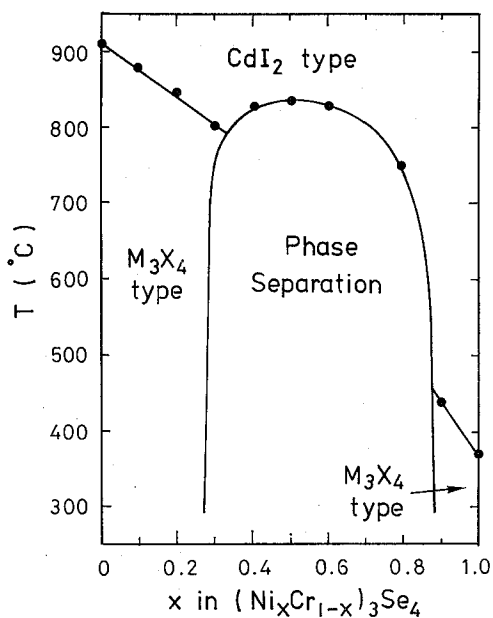
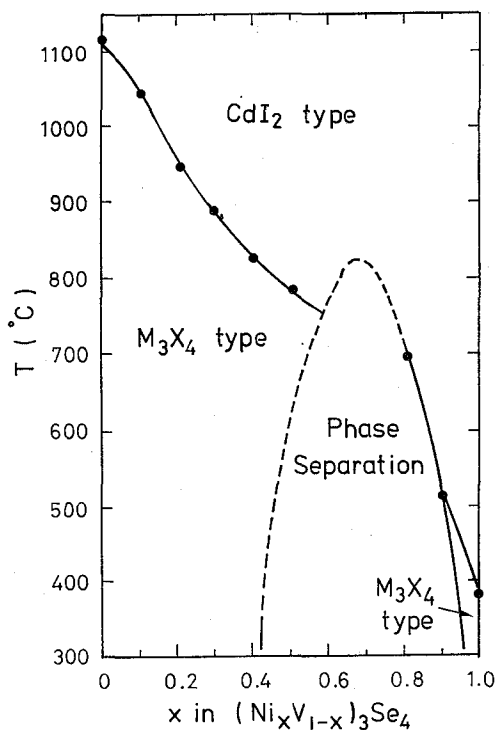


Fig. 15. Phase diagram of the $(\text{Ni}_x\text{Cr}_{1-x})_3\text{Se}_4$ system

4.12 $(\text{Ni}_x\text{V}_{1-x})_3\text{Se}_4$

We obtained the phase diagram shown in Fig. 16. Essentially, it resembles to

Fig. 16. Phase diagram of the $(\text{Ni}_x\text{V}_{1-x})_3\text{Se}_4$ system

those of the former two systems, and the phase separation range was $1/3 < x < 1$.

4.13 $(\text{Co}_x\text{Ti}_{1-x})_3\text{Se}_4$

In this system, the soluble region near Co_3Se_4 was very narrow. CdI_2 phase appeared in the composition range $0.1 < x < 0.3$. M_3X_4 phase and CdI_2 phase coexisted in the composition range $0.3 < x < 1.0$ at low temperature. Figure 17 shows a tentative phase diagram of the $(\text{Co}_x\text{Ti}_{1-x})_3\text{Se}_4$ system. Though the compound CoTi_2Se_4 has been reported to have the Cr_3S_4 -structure^{37,38}, our result showed that it has the CdI_2 -structure. This discrepancy seems to be caused by the thermal treatment.

4.14 $(\text{Ni}_x\text{Ti}_{1-x})_3\text{Se}_4$

No distinct thermal anomaly was detected in DTA except ones owing to the appearance of liquid phase. The results of the phase identification of the samples annealed at various temperatures were as follows. As in the case of the $(\text{Co}_x\text{Ti}_{1-x})_3\text{Se}_4$ system, the substitution of small amount of Ni for Ti suppresses M_3X_4 phase. On the other hand, the soluble region near Ni_3Se_4 was narrow. Figure 18 shows the temperature-product diagram. The phase transition to the CdI_2 -structure around 67°C in NiTi_2Se_4 reported by Plovnick *et al.*³⁹ was not detected in our DTA experiment.

Phase Diagram of $(M'_xM_{1-x})_3\text{Se}_4$ ($0 \leq x \leq 1$); ($M, M' = 3d\text{-transition metal}$)

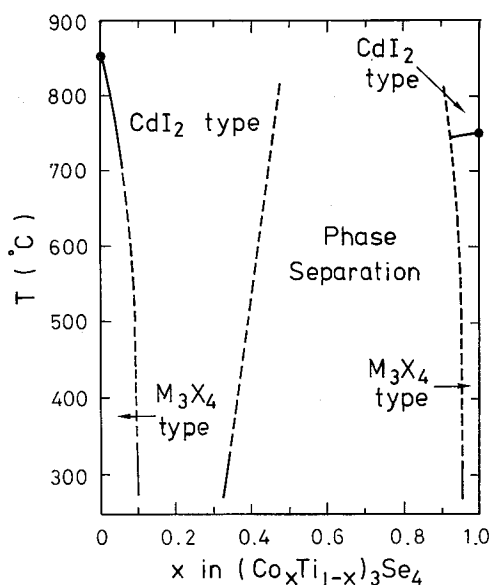


Fig. 17. Tentative phase diagram of the $(\text{Co}_x\text{Ti}_{1-x})_3\text{Se}_4$ system

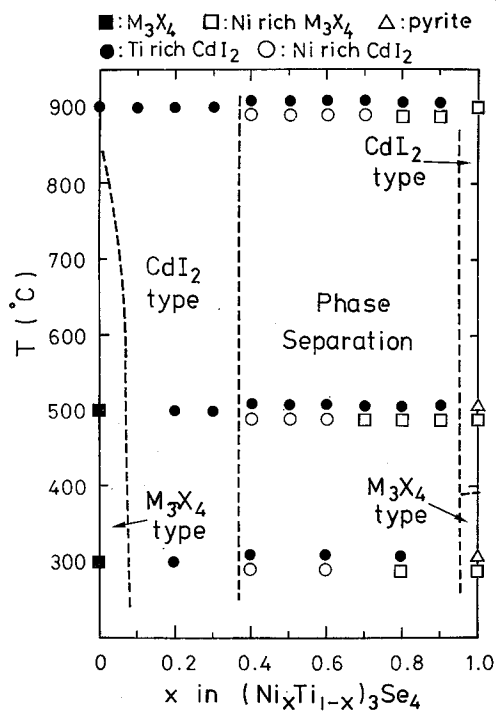


Fig. 18. Temperature-product diagram of the $(\text{Ni}_x\text{Ti}_{1-x})_3\text{Se}_4$ system. Paired symbols denote two phase mixture.

5. Electron microscopic observation

As shown in the previous sections, some systems exhibit the phase separation at low temperature. To investigate the feature of the phase separation, the electron microscopy was performed. The sample was $(\text{Co}_{0.6}\text{Cr}_{0.4})_3\text{Se}_4$ which was the mixture of two M_3X_4 phases at room temperature as seen in Fig. 14. First, the sample was cooled rapidly from 1050°C which is far above the upper limit of the phase separation. The X-ray diffraction patterns, however, showed those of the mixture of two M_3X_4 phases. A lattice image ([100] zone) of the sample is shown in Photo. 1. Dark and bright stripes with a width of about $90\text{--}120\text{ \AA}$ are aligned alternately and each stripe consists of about 20 parallel lattice fringes. From the closer analysis of the electron diffraction patterns and lattice images, it was confirmed that the two M_3X_4 phases with common a- and b-axis grow epitaxially along c-axis. The result of the X-ray diffraction in the $(\text{Co}_x\text{Cr}_{1-x})_3\text{Se}_4$ system revealed that the dark and bright stripes correspond to Co- and Cr-rich M_3X_4 phase, respectively. This indicates the feature of the phase separation by the anisotropic spinodal decomposition. Next, when the sample was reannealed in the phase separation region (800°C), it was perfectly separated into the two M_3X_4 phases with no common axis and no stripe was observed in the electron microscopic photographs.

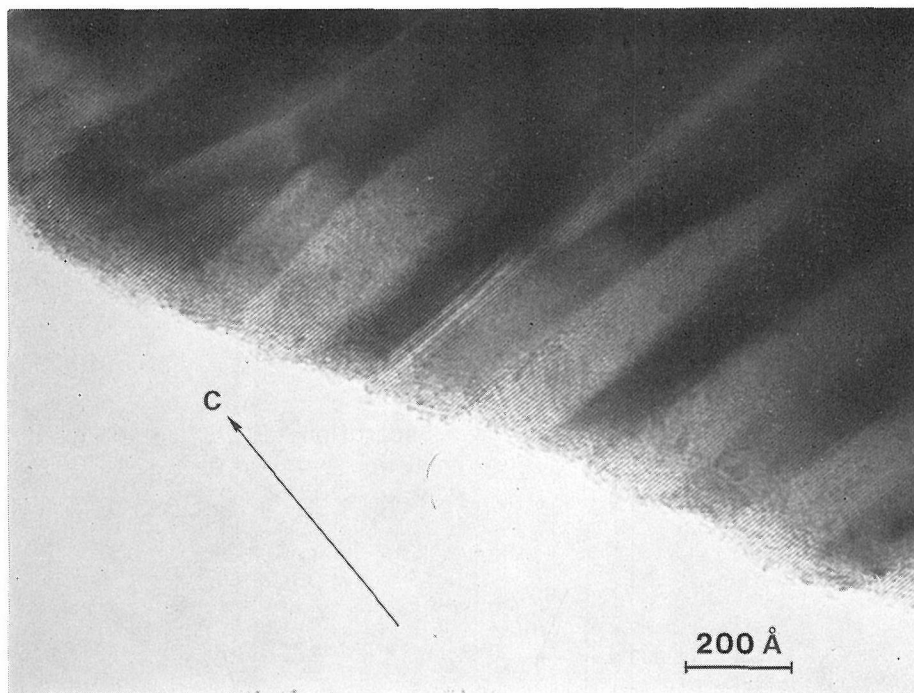


Photo. 1. Lattice image ([100] zone) of $(\text{Co}_{0.6}\text{Cr}_{0.4})_3\text{Se}_4$ cooled rapidly from 1050°C . Dark and bright stripes correspond to Co- and Cr-rich M_3X_4 phase, respectively (see text).

CONCLUDING REMARKS

The obtained phase diagrams of the $(\text{M}'_x\text{M}_{1-x})_3\text{Se}_4$ systems are classified into

Table III. Type of the phase diagram of the $(M'_xM_{1-x})_3\text{Se}_4$ system

M'	M	Type ^{a)}
V	Ti	S.S.
Cr	Ti	S.S.
Co	Ti	P.S.
Ni	Ti	P.S.
Cr	V	S.S.
Fe	V	S.S.
Co	V	S.S.
Ni	V	P.S.
Fe	Cr	S.S.
Co	Cr	P.S.
Ni	Cr	P.S.
Co	Fe	S.S.
Ni	Fe	S.S.
Ni	Co	S.S.

a) S.S.: solid solution, P.S.: phase separation.

two types; solid solution type and phase separation type, as shown in Table III. The systems of any two of Ti_3Se_4 , V_3Se_4 and Cr_3Se_4 , and also any two of Fe_3Se_4 , Co_3Se_4 and Ni_3Se_4 form a solid solution and exhibit the phase transition from the Cr_3S_4 - to CdI_2 -structure over a whole composition range. On the other hand, several systems of the former three and the latter three show the phase separation.

An anomaly in the T_c curve was observed in several systems of solid solution type. This anomaly may be due to the site preference of each metal ion or the metal-ordered structure as confirmed in the $(\text{Cr}_x\text{Ti}_{1-x})_3\text{Se}_4$ system^{30,31)} and in FeCr_2Se_4 .^{2,6)}

The systems of phase separation type are subdivided according to the phase separation region. In the $(\text{Co}_x\text{Cr}_{1-x})_3\text{Se}_4$ and $(\text{Ni}_x\text{Cr}_{1-x})_3\text{Se}_4$ systems, the phase separation region spreads around the middle composition, while that in the $(\text{Ni}_x\text{V}_{1-x})_3\text{Se}_4$, $(\text{Co}_x\text{Ti}_{1-x})_3\text{Se}_4$ and $(\text{Ni}_x\text{Ti}_{1-x})_3\text{Se}_4$ systems is in the composition range $1/3 < x < 1$. This suggests an intermediate compound at $x=1/3$ in the latter case. A probable compound is the compound with the metal-ordered structure such as $(\text{Ni})[\text{V}_2]\text{Se}_4$, $(\text{Co})[\text{Ti}_2]\text{Se}_4$ and $(\text{Ni})[\text{Ti}_2]\text{Se}_4$. The determination of the metal-ordered structure by neutron diffraction, Mössbauer spectroscopy or NMR is now in progress.

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