JOURNAL OF SOLID STATE CHEMISTRY 45, 411–412 (1982)

NOTE

Phase Diagram and Magnetic Properties of Cr_xTiSe_2 ($0 < x < 1$)

In the binary MX–MX_2 system (M: Ti, V, Cr, and X: S, Se), the NiAs-type structure appears at the composition MX and the CdI_2-type structure at MX_2. At intermediate compositions, metal vacancies are introduced in the alternate metal layers and at lower temperatures various kinds of vacancy-ordered structures form over a wide composition range. Two types of ordered structures, M_3X_4 and M_5X_8 type, were confirmed for V_xVS_2 (*1*), V_xVSe_2 (*1*), and Fe_xVS_2 (*2*) ($0 < x < 1$).

In this note, we report a phase diagram and some preliminary magnetic properties on the pseudobinary Cr–$TiSe_2$ system (Cr_xTiSe_2, $0 < x < 1$) as part of a series of investigations of the phase diagram and physical properties of M'_xMX_2 (M, M': 3d transition metal, $0 < x < 1$).

Samples were synthesized from high-purity elements, Cr (3N), Ti (3N), and Se (5N), by the method previously reported (*1*). The phase characterization at room temperature was made by electron and X-ray diffraction methods. The phase transition at higher temperatures was detected by high-temperature X-ray diffraction *in situ* (*2*) and also by DTA (differential thermal analysis) measurement.

Figure 1 shows a phase diagram obtained for Cr_xTiSe_2 in the temperature range from 200 to 800°C. In comparison with the phase diagram of V_xVS_2 and V_xVSe_2 (*1*), the general feature of the phase diagram has been altered mainly by the appearance of new phases with M_2X_3- ($2C_0$) (*3*), and M_8X_9-type structures, which may be considered to be inherited from the mother system Ti_xTiSe_2. In the case of V_xVS_2 and V_xVSe_2, M_5X_8 phase shows a successive phase transformation on heating of

$$M_5X_8\text{-} \rightarrow M_3X_4\text{-} \rightarrow CdI_2 \text{ type.}$$

From consideration of statistical thermodynamics (*4*), it was concluded that these phase transitions are of second order and the M_5X_8- to M_3X_4-type phase transition on changing composition at constant temperature is also of second order. In the Cr_xTiSe_2, however, it seems likely that all phase transitions except for M_3X_4 to CdI_2 type on heating are of first order. On samples very near to phase boundaries, two-phase coexistence was hardly detected by the X-ray diffraction method, but was observed sometimes by the electron diffraction method.

The temperature dependence of magnetic susceptibility (χ) was measured in the temperature range from 4.2K to room tempera-

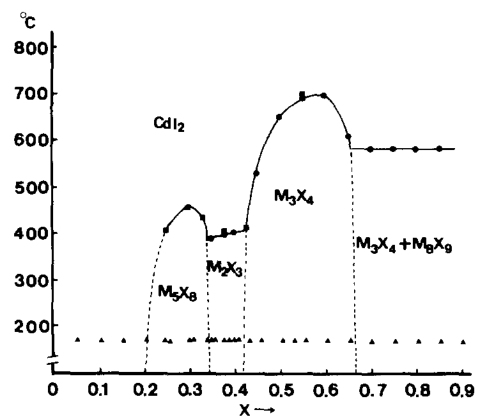

FIG. 1. Phase diagram of Cr_xTiSe_2 ($0 < x < 1$). ●: Detected by DTA. ■: Detected by high-temperature X-ray diffraction *in situ*. ▲: Prepared sample composition, samples were prepared in evacuated silica tube at 800°C for a week and then annealed at 300°C for 4 months.

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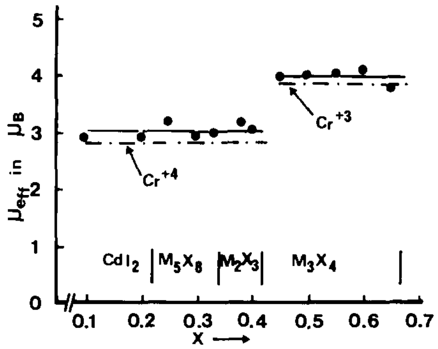

FIG. 2. Effective Bohr magneton number vs composition x in Cr_xTiSe_2. Dotted lines show the calculated μ_{eff} for Cr^{4+} and Cr^{3+} (spin-only value).

ture. At lower temperatures, χ of M_3X_4 phase showed anomalous temperature dependence, indicating magnetic ordering. Above 80K, all the samples prepared showed Curie–Weiss type χ–T behavior: $\chi = \chi_0 + C/(T - \theta)$. From the Curie constant C, the effective Bohr magneton number μ_{eff} was calculated on the assumption that only Cr ions have localized magnetic moment (*5*), disregarding the metal distribution. Figure 2 shows the composition dependence of μ_{eff}. Within experimental error, μ_{eff} is 3 μ_B in the CdI_2, M_5X_8, and M_2X_3 phases, and 4 μ_B in the M_3X_4 phase, which correspond to Cr^{4+} (μ_{eff} = 2.83 μ_B) and to Cr^{3+} (3.87 μ_B), respectively. This result is suggestive of the electronic state of Cr ions. It is impossible to discuss the valence state of Cr ions only from this result, because we have no information on electric properties or the distribution of Ti and Cr ions in crystals. However, it is likely that the electronic state of Cr ions is similar among the CdI_2-, M_5X_8-, and M_2X_3-type phases, and that of Cr ions in the M_3X_4-type phase is much different from that of other phases.

We are now investigating site distribution of Ti and Cr ions and also the detail of magnetic and electric properties for this system.

References

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2. Y. OKA, K. KOSUGE, AND S. KACHI, *Mater. Res. Bull.* **15,** 521 (1980).
3. In the course of this study, we could prepare a Ti_2Se_3 phase with a M_2X_3 ($2C_0$) -type structure for the first time.
4. Y. OKA, K. KOSUGE, AND S. KACHI, *J. Solid State Chem.* **24,** 41 (1978).
5. We confirmed that $TiSe_2$, Ti_5Se_8, Ti_2Se_3 ($2C_0$), and Ti_3Se_4 show temperature-independent weak paramagnetism.

N. OHTSUKA*
K. KOSUGE†
N. NAKAYAMA
Y. UEDA
S. KACHI

Department of Chemistry
Faculty of Science
Kyoto University
Kyoto, Japan

Received June 21, 1982

* Present address: Sumitomo Metal Industry, Central Research Laboratory, Amagasaki, Japan.
† To whom correspondence should be addressed.