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X-ray structural study of in-plane atomic arrangements in the layered compounds Cu_xTiS_2

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Abstract. X-ray diffuse intensity measurements have been performed at room temperature on the local arrangements of intercalated Cu atoms in the layered compounds Cu_xTiS_2 with compositions of $x = 0.13, 0.23, 0.32$ and 0.37 . Two types of diffuse maximum due to the different in-plane correlations of Cu atoms appeared, depending on the composition. For the lowest content of Cu atoms ($x = 0.13$), diffuse maxima appeared at $1/2, 0, 1/2, 0, 1/2, 1/2, 1/2, 1/2, 1/2$ and their equivalent positions. For the highest content of Cu atoms ($x = 0.37$), diffuse maxima appeared at $1/3, 1/3, 1/2, 2/3, 2/3, 1/2$ and their equivalent positions. In the cases of $x = 0.23$ and 0.32 , the two types of diffuse scattering coexist, with intensities depending on the composition. From the experimental results, we expect the following in-plane ordered structures for the low-temperature phases in the compounds $\text{Cu}_x\text{TiS}_2: 2 \times 2$ and $(\sqrt{3} \times \sqrt{3})R30^\circ$ structures in Wood notation, whose stoichiometric compositions x correspond to $1/4$ and $1/3$, respectively. The diffuse rods are modulated along the scan parallel to the $[001]^*$ direction centred on $1/2, 1/2, 0$ for $x = 0.13, 0.23$ and 0.32 and on $1/3, 1/3, 0$ for $x = 0.23, 0.32$ and 0.37 , with maxima appearing at every half-integer. This reveals an enhancement of the three-dimensional nature and a stacking sequence $\alpha\beta\alpha\beta \dots$ is deduced. Finally, the observed in-plane diffuse intensities are compared with the calculated ones, using a linearized mean-field approximation for the correlations of a binary Ising system well above T_c developed by Clapp and Moss.

1. Introduction

The layered disulphides of transition metals are intercalated with various ions and molecules between the sulphur layers which are normally separated through the Van der Waals interaction. These intercalation compounds are of interest because of their quasi-two-dimensional (2D) properties and because of their application as electrodes in cells. Inoue and Negishi measured the lattice constants a and c of M_xTiS_2 ($M = \text{V, Cr, Mn, Fe, Co}$ and Ni) grown by a chemical vapour transport technique over the whole concentration range $0 < x < 1$ systematically [1]. On the other hand, there are a few structural reports for Cu_xTiS_2 . Here, the space group of the host structure TiS_2 is $P\bar{3}m1$ with trigonal symmetry. As Cu atoms are intercalated between the sulphur layers randomly, the Cu_xTiS_2 has the same group as TiS_2 . Tazuke *et al* measured the composition dependence of the lattice parameters a and c for polycrystalline samples of Cu_xTiS_2 up to $x = 0.3$ [2]. The x-ray powder diffraction pattern shows a single phase with 1T-trigonal symmetry up to $x = 0.20$. Maruta *et al* have performed the x-ray diffraction study from a layered compound $\text{Cu}_{0.15}\text{Ti}_{1.08}\text{S}_2$ on the local structure of intercalants [3]. Weak diffuse scattering appears at $1/2, 0, 3/2, 1/2, 1/2, 3/2$ and $1, 1/2, 3/2$ in reciprocal space. Such a diffuse

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scattering along the scan parallel to $[001]^*$ direction on their positions was modulated, with maxima appearing at every half-integer. This reveals that both the intercalated copper atoms and self-intercalated titanium atoms are three-dimensionally correlated with each other and the stacking sequence $\alpha\beta\alpha\beta\dots$ is deduced. By analysing diffuse intensity, the Warren–Cowley short-range order (SRO) parameters were determined. A 2×2 in-plane ordered structure is expected for the low temperature phase, and the estimated in-plane and interlayer correlation lengths are about 12 Å. Recently, we have reported the composition dependence of the lattice parameters a and c for single crystals of Cu_xTiS_2 up to $x = 0.61$ [4]. The c -axis lattice constant increases gradually with increase of x and is about 3% larger at $x = 0.61$ compared with that for pure TiS_2 , though the a -axis lattice constant is almost constant for a whole range of composition.

In the present study, we have performed the x-ray diffraction study to measure composition dependences of diffuse scattering for single crystals of Cu_xTiS_2 compound up to $x = 0.37$ for understanding the local arrangements of the intercalated Cu atoms.

2. Experiment

The TiS_2 single crystals were prepared by the iodine transport method. The sample grew as thin crystals with the hexagonal shape. The average thickness of the crystals was 0.1 mm and their size in the hexagonal plane was 1 mm. The single crystals of Cu_xTiS_2 were prepared electrochemically by immersing TiS_2 crystals in an aqueous solution of 0.1 N CuSO_4 with Cu metal as the electrode. The composition of the compounds was controlled by changing an alternating current and composition of the solution [4]. The four specimens were, thus, obtained for the present experiments. The compositions of the samples used were determined to be $x = 0.13, 0.23, 0.32$ and 0.37 by the electron probe microanalysis (EPMA) method. Uncertainty for the composition is less than ± 0.01 . The x-ray measurements were performed with the use of a four-circle diffractometer on a rotating anode generator (RU-300) at room temperature, where a flat graphite monochromator was utilized to obtain the $\text{Mo K}\alpha$ radiation. The scattered intensities were collected by a scintillation counter. Both mosaic spreads of pure TiS_2 and the intercalated compound parallel to the $[001]^*$ direction are approximately 0.50 degrees, using estimates of the full width at half maximum (FWHM) of the 004 Bragg reflection. A θ - 2θ scan parallel to the $[001]^*$ direction through the $00l$ reflections was taken at room temperature with the reflection geometry to confirm the average structure of the sample. There were no additional reflections on the $00l$ patterns, i.e. stage 1 only exists. A detailed x-ray determination of the atomic displacements in the compounds Cu_xTiS_2 is reported in a separate paper [5]. X-ray diffuse intensities were observed on the several reciprocal lattice planes and several directions for the four specimens.

3. Results and interpretation

The diffuse intensity distributions for all the four specimens are shown on the $(h,k,1/2)$ reciprocal lattice plane in figure 1, where the raw background and the fundamental reflections were subtracted. The legend of the relative intensity values is shown in the figure. As seen from the figures, we can understand that there are two types of diffuse scattering for the maximal positions; at $1/2, 1/2, 1/2$ and its equivalent positions and at $1/3, 1/3, 1/2$ and its equivalent ones. The former can be seen in figure 1(a) and (b) and the latter in figure 1(c) and (d). These reveal that the copper atoms are correlated with each other in the intercalated plane. Figure 2 shows the diffraction profiles, which correspond to the one-dimensional scan along the $[110]^*$

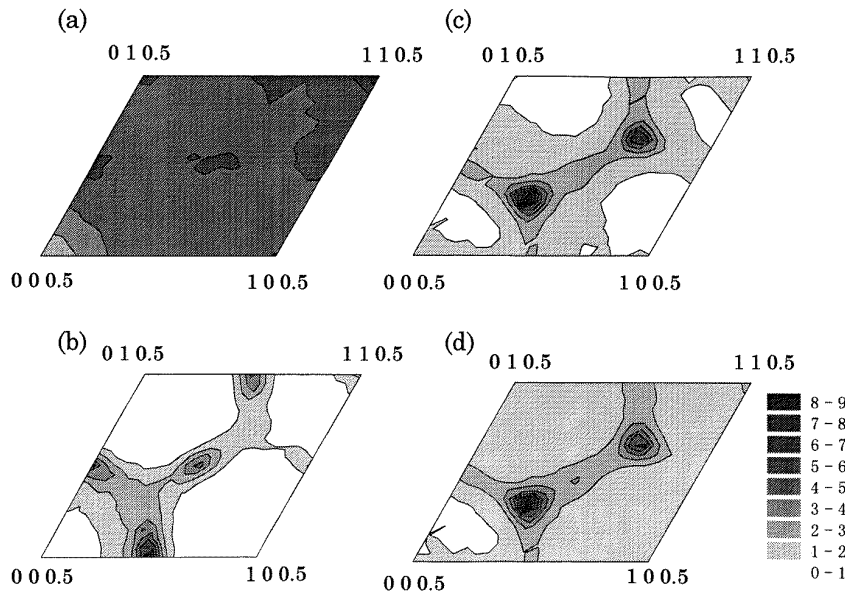


Figure 1. Diffuse intensity distribution on the $(h,k,1/2)$ reciprocal lattice plane for the specimen of (a) $x = 0.13$, (b) $x = 0.23$, (c) $x = 0.32$ and (d) $x = 0.37$.

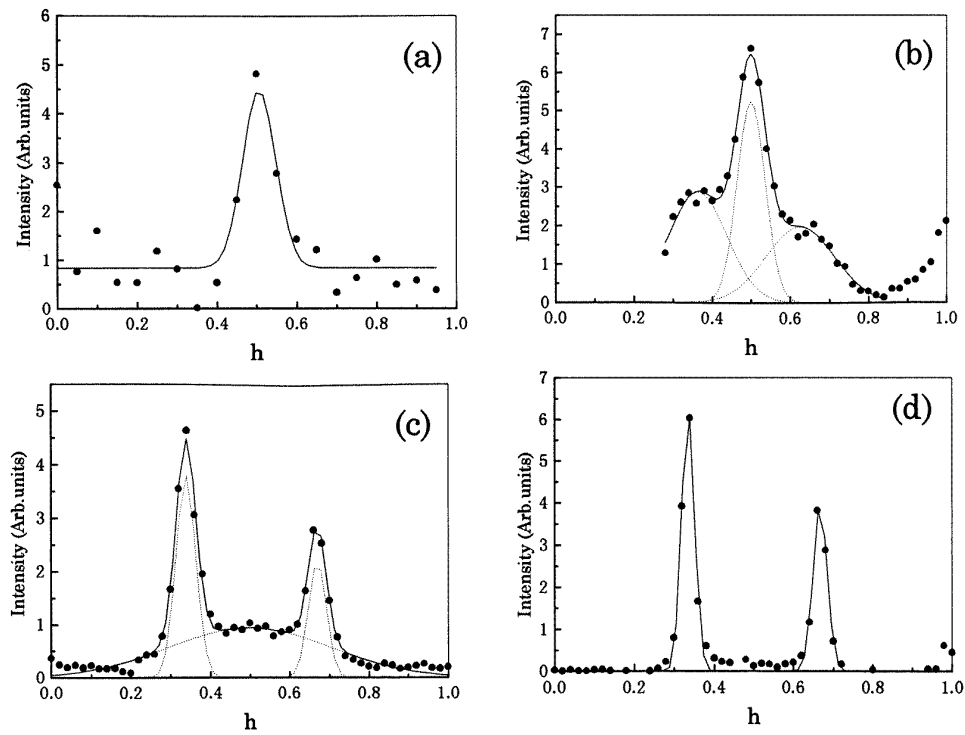


Figure 2. Diffuse intensity distribution along the $[110]^*$ direction from $0,0,1/2$ to $1,1,1/2$ reciprocal lattice points for the specimens of (a) $x = 0.13$, (b) $x = 0.23$, (c) $x = 0.32$ and (d) $x = 0.37$. Dotted curves were obtained with the use of the three profiles fitting procedure.

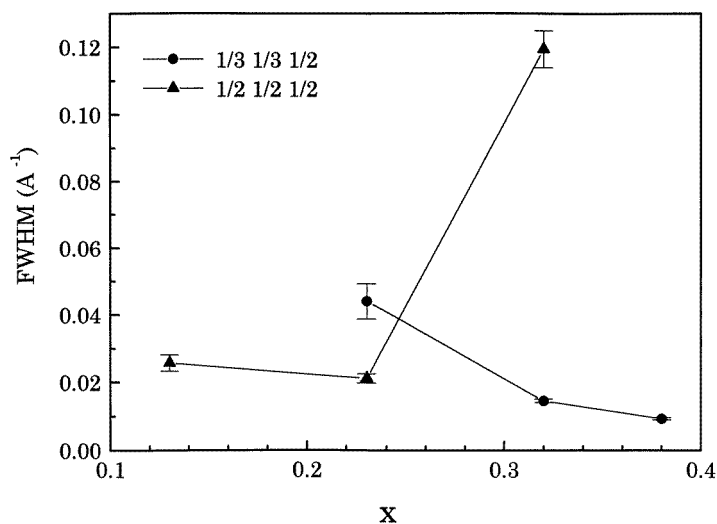


Figure 3. Intralayer correlation lengths obtained from the FWHM of diffuse scattering along the $[110]^*$ direction at $1/2, 1/2, 1/2$ and $1/3, 1/3, 1/2$ points.

direction from $0,0,1/2$ to $1,1,1/2$. In the figures, dotted curves were obtained with the use of the fitting procedure with Gaussians. In particular, three profiles were used for figures 1(b) and (c). The value of the FWHM for each diffuse scattering along the $[110]^*$ direction was obtained from figure 2 to estimate the in-plane correlation length and are shown in figure 3. In this calculation, we did not consider the instrumental broadening, because it is small compared with that for the diffuse intensity profile. Though there are a few data points, it is thought that near the stoichiometric compositions ($x = 1/4$ and $1/3$) the value of the FWHM is relatively small. This means that the in-plane correlation length at the composition is larger than that at a nonstoichiometric one. Possible in-plane atomic arrangements for the compounds will be discussed in the following section.

Figure 4 shows the diffuse intensity distributions parallel to the $[001]^*$ direction at $1/2, 1/2, 0$ and on $1/3, 1/3, 0$ for $x = 0.13, 0.23, 0.32$ and 0.37 . Both diffuse maxima appear at every half-integer, except for figures 4(d) and (e). It is assumed that the scatterings originate from correlation between intercalated atoms with three-dimensional nature having a stacking sequence $\alpha\beta\alpha\beta\dots$

4. Discussion

We have realized from the present study that x-ray diffuse scattering measurements give useful information about the structural fluctuations of the intercalants in the compounds. In the 19th chapter of Kittel's textbook [6], surface nets of adsorbed atoms on the lattice are shown for four types of two-dimensional lattice. In particular, there are three possible surface structures for hcp(0001) and fcc(111) planes: 2×2 , $(\sqrt{3} \times \sqrt{3})R30^\circ$ and 1×1 with the use of Wood notation, where ideal compositions of adsorbed atoms are $1/4$, $1/3$ and 1 for the mother lattices, respectively. We here estimate the in-plane arrangements of Cu atoms based on the experimental results of the diffuse scattering patterns on the $(h,k,1/2)$ reciprocal plane. In the lower content of Cu atoms, a 2×2 in-plane structure is expected for the low temperature

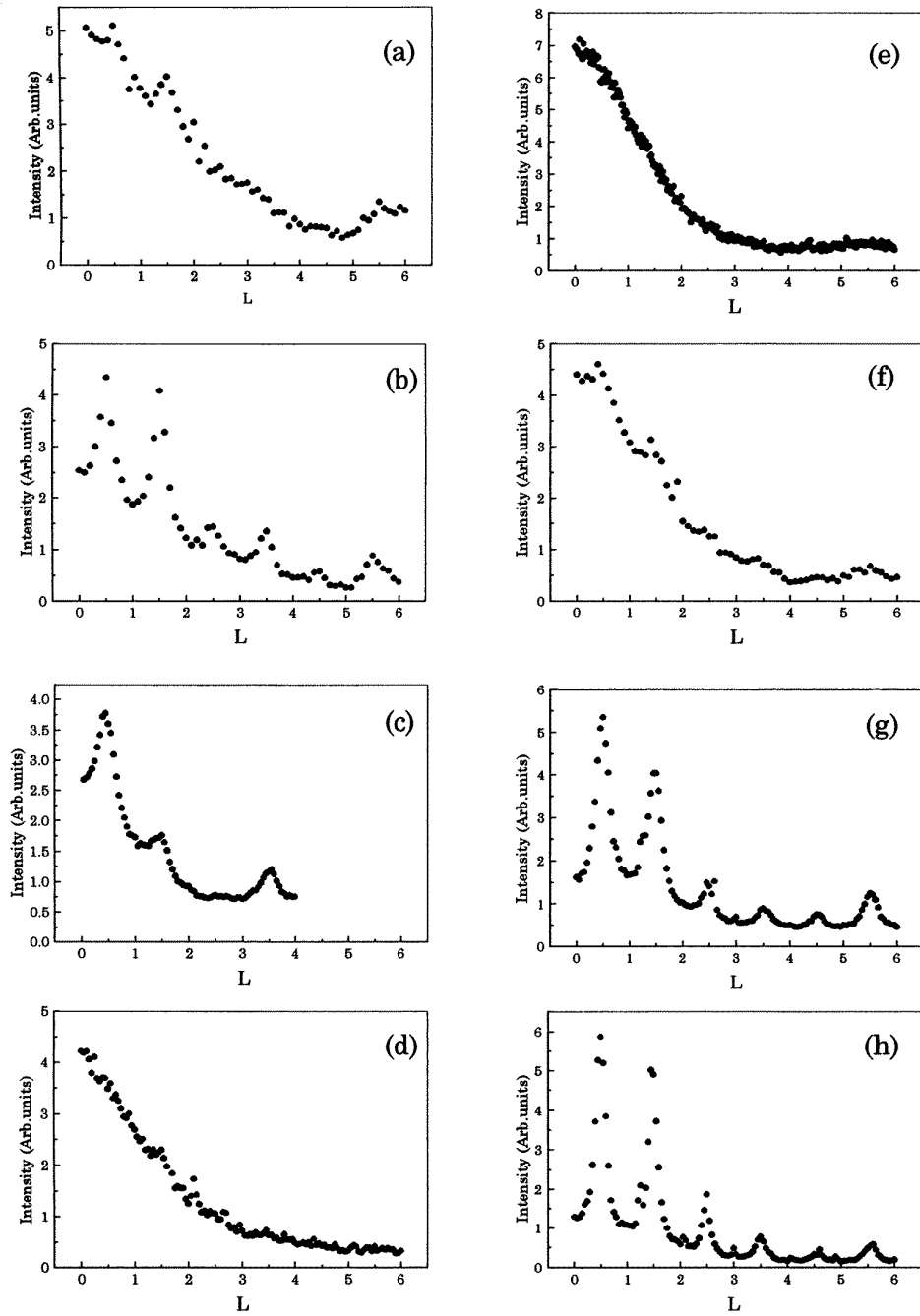


Figure 4. Diffuse intensity distributions parallel to the $[001]^*$ direction at $1/2, 1/2, 0$ ((a)–(d)) and $1/3, 1/3, 0$ ((e)–(h)) from the specimen of $x = 0.13, 0.23, 0.32$ and 0.37 , respectively.

phase due to appearing the diffuse maxima at $1/2, 0, 1/2$, $0, 1/2, 1/2$, $1/2, 1/2, 1/2$ and their equivalent positions. In the composition of around $x = 1/3$, a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure

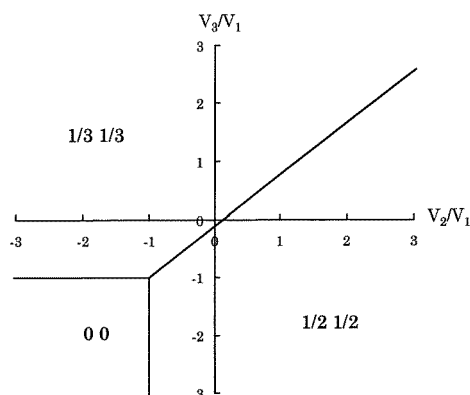


Figure 5. Existence regions of the three structure types. Horizontal and vertical axes correspond to V_2/V_1 and V_3/V_1 ratios when the sign of V_1 is positive.

is expected for the ordered structure because the diffuse maxima appear at $1/3, 1/3, 1/2$ and its equivalent position. In the higher content of Cu atoms, diffuse maxima are expected to appear around the Bragg reflections. We have, therefore, prepared the single crystal of $x = 0.61$ and tried to observe such diffuse scatterings on the pattern. Except for thermal diffuse scattering, no significant diffuse scattering was observed. However, the system Cu_xTiS_2 is an ideal material to understand successive in-plane atomic arrangements for the layered compound.

In a linearized mean-field approximation for the correlation function of a binary Ising system, developed by Clapp and Moss [7], the SRO diffuse scattering intensity is expressed by

$$I^{SRO}(\mathbf{k}) = C / \{1 - T_c V(\mathbf{k}) / T V(\mathbf{k}_m)\} \quad (1)$$

where $V(\mathbf{k})$ is a Fourier transform of the pair interaction potential $V(\mathbf{r}) = (1/2)\{V^{CuCu}(\mathbf{r}) + V^{\square\square}(\mathbf{r}) - 2V^{Cu\square}(\mathbf{r})\}$, between pairs of atoms separated by a vector \mathbf{r} . T_c is the critical temperature and C is a normalization constant. The symbol \square means a vacancy. If the sign of $V(\mathbf{r})$ is negative, there is a preference for unlike neighbours, i.e. Cu–vacancy pairs. On the other hand, if it is positive, there is a preference for like neighbours, i.e. Cu–Cu and vacancy–vacancy pairs. $V(\mathbf{k}_m)$ is the minimum value of $V(\mathbf{k})$ at $\mathbf{k} = \mathbf{k}_m$, where \mathbf{k}_m corresponds to a superlattice point in the ordered reciprocal space. When \mathbf{k} is approaching to \mathbf{k}_m , the maximum value of $I^{SRO}(\mathbf{k})$ appears at the point. This expression has been successful well above T_c in evaluating ratios of interaction energies for a two-dimensional system [8]. We, therefore, try to obtain values of the pair interaction potential ratios which give the diffuse maximum at $0, 0, 0$, $1/2, 0, 0$ or $1/3, 1/3, 0$. In the calculation, potentials up to the third-nearest neighbour are introduced and V_1 is assumed to be positive due to the physical meaning. Figure 5 shows the existence regions for the three structures as functions of the ordering energy ratios V_3/V_1 and V_2/V_1 when the sign of V_1 is positive. It is characteristic that the 1×1 , 2×2 and $(\sqrt{3} \times \sqrt{3})R30^\circ$ ordered structures appear with depending on two potential ratios. The intensity distributions of $I^{SRO}(\mathbf{k})$ as functions of V_2/V_1 and V_3/V_1 are calculated, assuming $T_c/T = 0.9, 0.5$ and 0.1 . We have compared the shape of the diffuse intensity, thus calculated, with the observed one. In figure 6(a), diffuse maxima at $1/2, 0, 0$ and its equivalent positions are clearly seen with the ratios $V_2/V_1 = 0.1$ and $V_3/V_1 = -1.0$ when T_c/T is equal to 0.9 . In figure 6(b), diffuse maxima at $1/3, 1/3, 0$ and its equivalent positions are seen with the ratios $V_2/V_1 = -0.5$ and $V_3/V_1 = 0.1$ when T_c/T is equal to 0.9 . Agreements between the calculated and observed intensity distributions are fairly

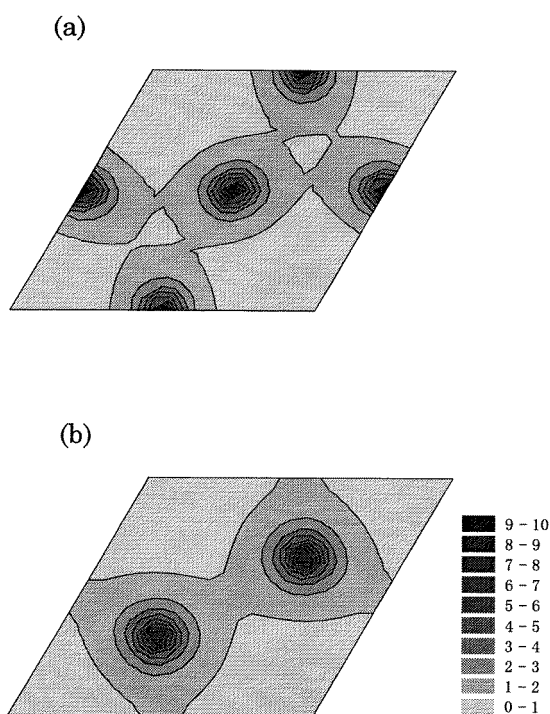


Figure 6. Calculated short-range order diffuse intensity distributions with the use of equation (1) in the text, assuming $T_c/T = 0.9$: (a) $V_2/V_1 = 0.1$ and $V_3/V_1 = -1.0$ and (b) $V_2/V_1 = -0.5$ and $V_3/V_1 = 0.1$.

good. We are now planning to perform the x-ray diffuse scattering intensity measurements below room temperature to investigate whether an ordered structure exists or not.

It is also peculiar that two types of diffuse scattering exist at the nonstoichiometric composition region of the Cu atoms and that the relative diffuse maxima between the two depend on the composition. In our previous papers on Cu–Pt and Pd–Mn alloys which show the face-centred cubic structure above the critical temperature, two types of diffuse maximum have been observed and their intensities also depend on the composition [9–11]. Though we have proposed three-dimensional correlated structures of constituent atoms in alloys, there are no reports to understand such structural fluctuations from a theoretical point of view. We expect that the phase stability should be calculated for both alloy systems and the compounds Cu_xTiS_2 from the thermodynamical treatment.

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