6 Crystallography

6-1 How Does the Accuracy of a Continuous Phase Transition Temperature Depend on the Angular Resolution of a Powder Diffractometer?

A number of researchers have studied structural phase transitions in various materials, since this is one of the most important topics in many fields such as physics, chemistry, biology, geoscience and materials science. Near the transition temperature, many materials exhibit interesting and useful properties. Therefore, it is exceedingly important to determine accurate transition temperatures [1, 2]. Most materials do not exist as not single crystals, but as polycrystalline compounds or powders. The precision of unit-cell parameters can be improved by using higher-resolution powder diffractometers [1-4]. Therefore the precision of transition temperature measurements can also be improved by using a higher-resolution instrument. However, to the best of our knowledge, the effect of angular resolution on the accuracy of transition temperature measurements has not been reported in the literature, although it is very important from the viewpoint of science and technology.

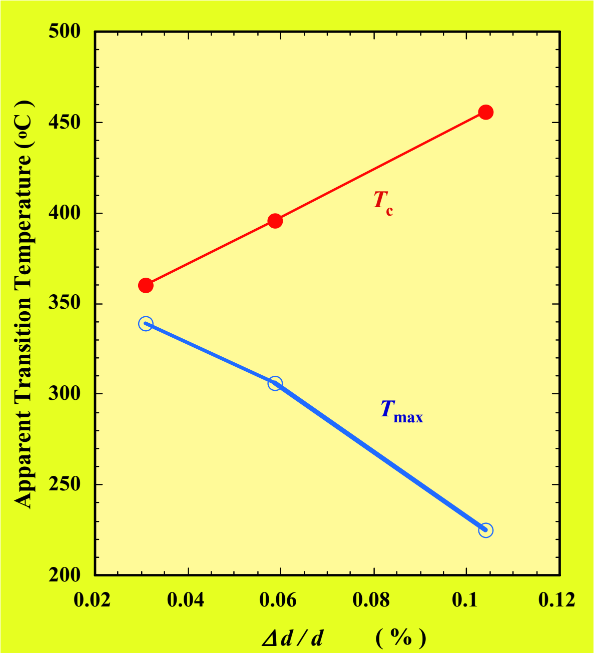

Figure 1
Relationship between resolution ($\Delta d/d$) and apparent transition temperatures. Open circles denote the maximum temperature at which the peak splitting due to the 400 and 040 reflections is detectable. Closed circles denote the transition temperature determined by power-law fits.

Here we have investigated *in situ* a continuous transition between the orthorhombic and tetragonal phases in perovskite-structured $La_{0.64}(Ti_{0.92},Nb_{0.08})O_3$ using three X-ray powder diffractometers with different $\Delta d/d$ resolutions of 0.03%, 0.06% and 0.10% [2]. d and Δd denote $\lambda/(2\sin\theta)$ and peak width where λ and θ represent X-ray wavelength and Bragg angle. This compound was chosen for study because it exhibits a continuous transition and the peak splitting is very small near the transition point [1, 4]. Synchrotron X-ray powder diffraction data with $\Delta d/d$ resolutions of 0.03% and 0.06% were collected at BL-3A. A small furnace developed by Tanaka [5] was utilized for high-temperature synchrotron powder-diffraction measurements. Low-resolution data of $\Delta d/d$ = 0.10% was collected with a conventional Cu$K\alpha$ diffractometer (Bragg-Brentano geometry). The peak profiles of the 400 and 040 reflections were measured at different temperatures with the three diffractometers.

The maximum temperature where the split between the 400 and 040 peaks is detectable, T_{max}, is plotted against the $\Delta d/d$ resolution as open circles in Fig. 1. T_{max} was found to be 339ºC, 306ºC and 225ºC for $\Delta d/d$ reso-

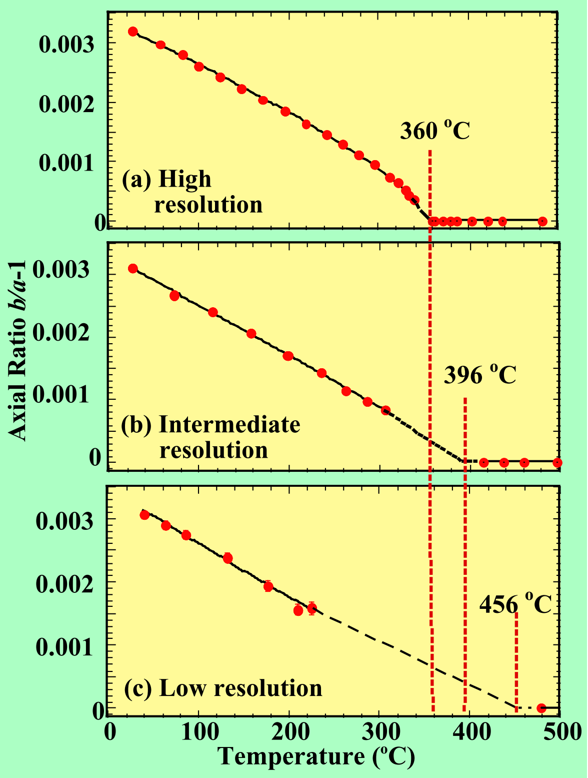

Figure 2
Temperature dependence of the axial ratio b/a–1 determined by (a) high-, (b) intermediate-, and (c) low-resolution diffractometers of $\Delta d/d$ = 0.03%, 0.06% and 0.10%. Solid lines are least-squares fits to the experimental data using a power law. The dashed lines are extrapolations of their fits.

lutions of 0.03%, 0.06% and 0.10%, respectively. T_{max} increases with decreasing $\Delta d/d$ value. The transition temperature is often estimated by T_{max} in the literature. The large spread in the T_{max} measurements of 114°C clearly shows the importance of high angular resolution for accurate determination of transition temperatures.

In the orthorhombic phase the axial ratio *b/a* of the cell parameters decreased with increasing temperature and the *b/a* ratio became unity at the transition point (Fig. 2). The transition temperature T_c was calculated by applying a power law $b/a-1=C(1-T/T_c)^\beta$ to data taken at temperatures where the peak split is detectable. *C* and β are a coefficient independent of temperature and the critical exponent, respectively. T_c was estimated to be 456±228°C, 396±14°C and 360±2°C for low-, intermediate-, and high-resolution data, respectively. Thus, the T_c decreases with decreasing of $\Delta d/d$ value and with increasing angular resolution (Fig. 1). It is worth noting that a change of angular resolution from 0.10% to 0.03% considerably improves the accuracy from ±228°C to ±2°C. This finding also indicates the importance of high angular resolution in powder diffractometry for the accurate determination of transition temperatures.

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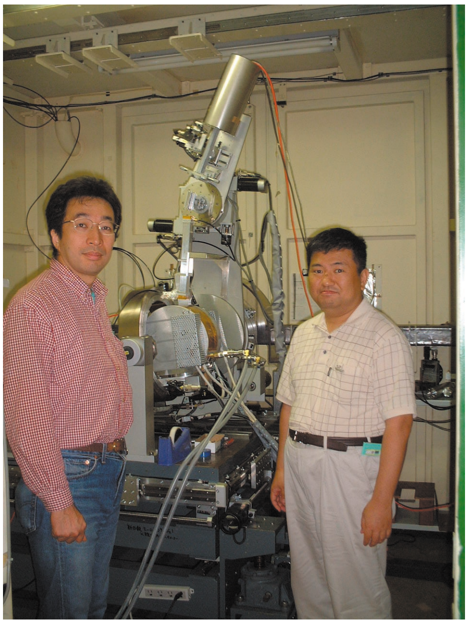

High-temperature synchrotron X-ray powder diffraction experiment at BL-3A.

6-2 Structure Determination of Spinel-Type $CuIr_2S_4$ at Low Temperature from High-Resolution Powder Diffraction Data

Spinel compounds have been studied for many years because they exhibit a large variety of physical properties. The cubic spinel structure has two crystallographically different sites; tetrahedral (A) and octahedral (B) sites occupied by cations and anions. The B site forms a corner sharing tetrahedral network, which causes geometrical frustration when occupied by mixed valence ions or magnetic atoms. In this case, some kind of ordering such as charge-ordering often occurs at low temperatures and interesting physical properties are revealed.

Spinel sulfide $CuIr_2S_4$ is one example of such a material. This compound has attracted attention in the last decade because of its unusual properties; a sharp metal-insulator transition (MIT) at T_{MI} = 226 K accompanied by a structural transition [1]. Experimental results [2,3] show that the low-temperature insulating phase is non-magnetic and that the Cu ion is monovalent, meaning that the average valence of the Ir ions is 3.5. Therefore, the mechanism of MIT was considered to be made up from a charge-ordering of Ir^{3+} (spin $S = 1/2$) and Ir^{4+} ($S = 0$), and possibly some kind of spin dimerization for Ir^{4+}. It is important to determine the precise crystal structure of the low-temperature phase to understand the nature of the transition. Conventional X-ray diffraction experiments have been tried to achieve this. However, not only did numerous weak superlattice peaks appear, but also the splitting for some peaks was too small to resolve (Fig. 3), and it was difficult even to determine the lattice symmetry.

A synchrotron radiation X-ray powder diffraction experiment was carried out using the high-resolution diffractometer installed at BL-3A. The wavelength used was 1.5470 Å, and a flat Si(111) crystal analyzer was used in order to obtain high angular resolution. Using these optics, the full width at half maximum of the respective peaks in the low 2θ region was less than 0.02°. From careful observation of the peak splitting of the fundamental reflections (Fig. 3), the lattice symmetry is found to be triclinic [4] and the lattice parameters estimated to be a = 9.689 Å, b = 9.717 Å, c = 10.026 Å, α = 90.050°, β = 90.025° and γ = 90.083° assuming a pseudo cubic axis. All peaks including the super-lattice and forbidden reflections were indexed and the unit cell converted so as to have translational symmetry. Next, the initial structural parameters were constructed by combining the results of electron and neutron diffraction data. Starting from the initial model, Rietveld analysis was performed to determine the precise structural parameters. As a result, a very interesting structure was obtained [5]. As shown in Fig. 4, the Ir sub-lattice was found to consist of two types of Ir bicapped hexagonal rings, which were described as

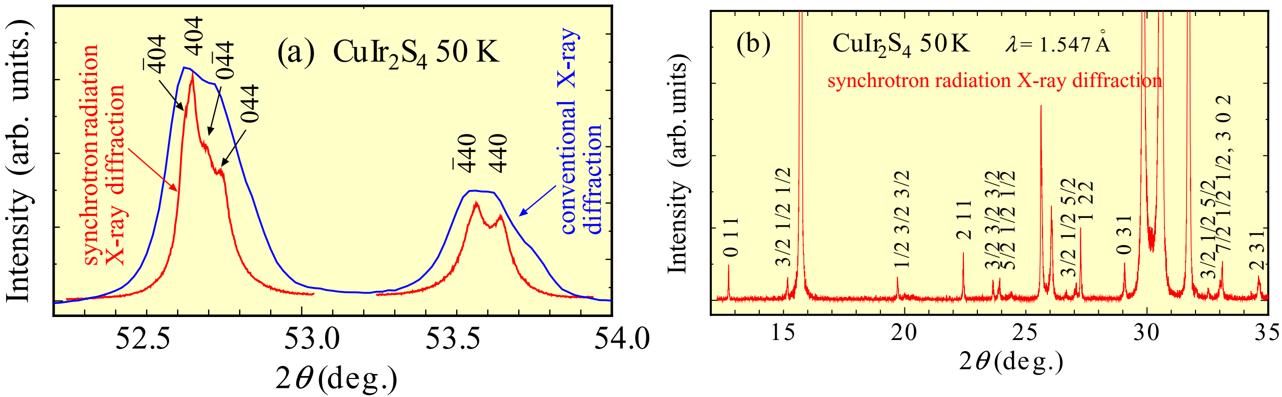

Figure 3
(a) The profiles of 440 fundamental reflections of $CuIr_2S_4$ at 50 K obtained by synchrotron radiation X-ray and conventional X-ray diffraction. The indices are based on the pseudo cubic axis. (b) The same diffraction pattern as (a). Numerous super-lattice and forbidden reflection peaks appear.

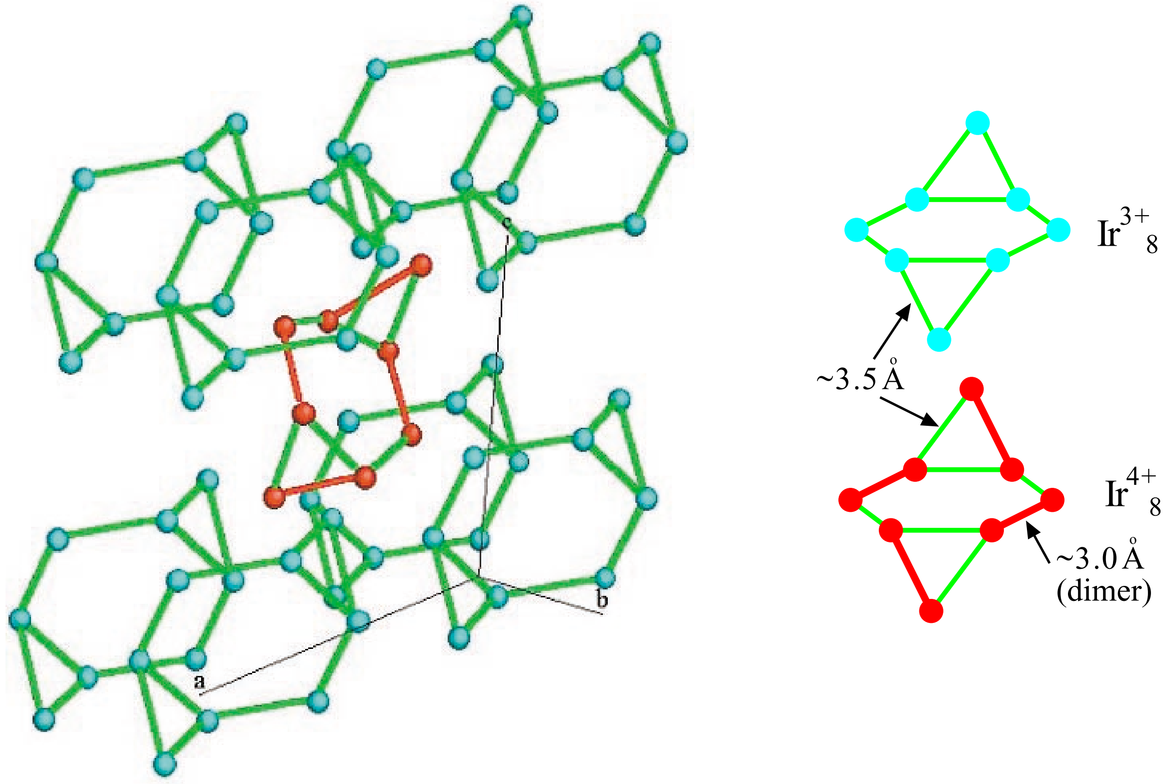

Figure 4
The crystal structure of the low temperature phase of $CuIr_2S_4$, where the configuration of the Ir ions is shown. Blue and red circles indicate the Ir^{3+} and Ir^{4+} ions and the dimerized Ir-Ir bonds are shown as red cylinders.

Ir^{3+}_8 and Ir^{4+}_8 octomers. Further, the Ir^{4+} ions with $S = 1/2$ are found to form dimers. The Ir-Ir distance in the dimers is ~3.0 Å, while all the other Ir-Ir nearest-neighbor distances were ~3.5 Å. The crystal structure obtained by the present study strongly supports the thesis that $CuIr_2S_4$ undergoes a simultaneous charge-ordering and spin-dimerization transition.

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