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The structure of *Y*-$Al_{13-x}Co_4$ ($x = 0.8$) analyzed by single crystal X-ray diffraction coupled with anomalous X-ray scattering

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ABSTRACT

The structure of Y-$Al_{13-x}Co_4$ ($x = 0.8$) has been analyzed by single crystal X-ray diffraction: space group $C2/m$ (No.12), $a = 17.0525\ (20)$ Å, $b = 4.1059(6)$ Å, $c = 7.5047(9)$ Å, $\beta = 116.01(1)^\circ$. Y-$Al_{13-0.8}Co_4$ is isostructural with a ternary Y-$Al_{13-x}(Co,Ni)_4$ and crystallized at the Al-poor region close to $Al_{13}Co_4$. The distribution of Co was also confirmed by anomalous X-ray scattering (AXS) at Co K absorption edge. Present analysis revealed the Co distribution at Co(1) and Co(2) sites, only, by suggesting unique pentagonal atomic columns with a period of 4 Å different from that observed in $Al_{11}Co_4$.

1. Introduction

According to a cluster model designed for quasicrystals, the structures of decagonal quasicrystals as well as their approximants are interpreted as two-dimensional atomic arrangements by considering the definite linkages of columnar structures. Therefore, structural models for the decagonal quasicrystals frequently use the local atomic configuration of crystalline approximants close in chemical composition. The Al-rich part of the binary Al–Co alloy system indicates several interesting crystalline phases and for examples, there are striking similarities between the local structure of the monoclinic $Al_{13}Co_4$ and that of decagonal phases in the Al–Co–Ni and Al–Co–Cu systems [1–3]. In the composition area between the established Al_9Co_2 and Al_5Co_2 [4], we find four structures with very close chemical compositions; monoclinic $Al_{13}Co_4$ (M-$Al_{13}Co_4$) [3], orthorhombic $Al_{13}Co_4$ (O-$Al_{13}Co_4$) [5,6], Y-phase and Z-phase (so-called τ inflated -$Al_{13}Co_4$) [7] and more recently, anther monoclinic $Al_{11}Co_4$ was reported [8]. Similarity in a–c plane structures is found in these five crystalline phases besides the composition $Al_{13}Co_4$. Nevertheless, the b-axis of Y-phase ($b = 4.10$ Å) and $Al_{11}Co_4$ ($b = 4.05$ Å) are about half of those of the others. In this context, the structure of Y-phase and $Al_{11}Co_4$ are suggested to serve the typical columnar structural unit for the Al–Co decagonal phases with a period of 4 Å, in particular. This prompts us to study the structure of the binary Y-phase for the first time. This paper reports the structural analysis of Y-$Al_{13-x}Co_4$ ($x = 0.8$), by using ordinary single crystal X-ray diffraction coupled with the anomalous X-ray scattering at the Co K absorption edge.

2. Experimental

An alloy ingot of $Al_{71}Co_{19}$ was prepared from pure metals of Al (99.999%) and Co (99.99%) by using a conventional arc furnace in an Ar atmosphere. A solidified ingot was charged in an Al_2O_3 crucible and sealed into an evacuated silica glass tube. This sample tube was heated at 1180 °C for 24 h then cooled down to 1130 °C with a speed of 10 °C/h. After the subsequent annealing at 1130 °C for 48 h, the alloy sample was quenched in ice water. Many needle-like crystals with more than 30 μm in size were obtained in the prepared sample and electron probe microanalysis (EPMA; JEOL JXA-8621MX) indicated that the chemical composition of such needle crystals was Y-phase $Al_{75.5}Co_{24.5}$, which was apparently rich in Co content in comparison with that of $Al_{13}Co_4$ [7]. Single crystal sample of the Y-phase was cut out from the annealed sample and used for the X-ray examinations. Intensity data sets for the ordinary structural analysis were collected in the ω-2θ scan mode on an AFC7R (Rigaku) four-circle diffractometer by using monochromated Mo *Ka* radiation ($\lambda = 0.71073$ Å). After Lorentz and polarization corrections, an absorption correction was performed by using an integration method with an isometric grid, ACACA [9]. For the ordinary X-ray diffraction analysis, the least-squares software of SHELXL-97 [10] was used together with the atomic scattering factors provided by the International Tables for Crystallography [11]. The cell parameters of $a = 17.0525(20)$ Å, $b = 4.1059(6)$ Å, $c = 7.5047(9)$ Å, $\beta = 116.01(1)^\circ$ were obtained by the least-squares calculation applied to the 25 well centered 2θ values between 35.4° and 39.5°. Experimental details for the measurements of Mo Kα radiation were summarized in Table 1 together with the final results. It should be added that the fine needle-

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Table 1
Experimental data of Y-$Al_{13-x}Co_4$ ($x = 0.8$).

Chemical composition (EPMA)	$Al_{24.7}Co_8$
Chemical composition (X-ray)	$Al_{24.42(2)}Co_8$
Temperature (K)	298(2)
Wavelength (Å)	0.71069
Space group	$C2/m$
Unit cell (Å)	$a = 17.0525(20)$
	$b = 4.1059(6)$
	$c = 7.5047(9)$
	$\beta = 116.010(12)$
Volume (Å^3)	472.23(10)
D_x (Mg/m^3)	3.971
Absorption coefficient (mm^{-1})	7.976
F (0 0 0)	533
Crystal size (mm^3)	$0.06 \times 0.03 \times 0.03$
$2\theta_{max}$ (°)	69.90
R_{sigma}	0.0286
R_{sigma}	0.0266
h,k,l	$-20 < h < 27$, $-6 < k < 0$, $-10 < l < 12$
No. of measured reflections	1223
No. of independent reflections	1151
No. of observed reflections	954
No. of parameters	57
Weighing scheme	$1/[\sigma^2(F_{obs}^2) + (0.0211P)^2 + 0.4708P]$
Goodness-of-fit on F^2	1.215
Final R indices [$I > 2\sigma(I)$]	0.0288
Final $wR2$ indices (all data)	0.0660
Largest diff. peak and hole (electron/Å^3)	0.905 and −0.643

$P = (F_o^2 + 2F_c^2)/3$.

like crystalline phase, which is quite similar to that of $Al_{13}Co_4$ ($Al_{76.6}Co_{23.4}$), was also found in the present sample. Nevertheless, the obtained crystals were not large enough for the single crystal structural analysis.

The AXS measurements were carried out at the BL-10A station of synchrotron radiation, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Japan. A pair of incident energies used in the present AXS measurements were 7.560 keV and 7.685 keV, which correspond to 150 eV and 25 eV below the Co K absorption edge (7.710 keV). These energies were tuned by using a Si (1 1 1) monochrometor and details on the experimental setup including the data processing are almost similar to the previous analysis [12,13]. Intensity data up to about $\sin\theta/\lambda = 0.48$ for each energy were measured on a vertical-type four-circle goniometer in the ω–2θ scan mode. Number of the measured reflections for the X-ray incidences of 7.560 keV and 7.685 keV are 861 and 852, respectively. After averaging equivalent reflection pairs, 242 reflection pairs were selected and employed for the present AXS analysis. Low X-ray energies at Co K absorption edge and the limited beam time of a synchrotron radiation source could not allow us to obtain the AXS data with a resolution equivalent to that by Mo Kα radiation. Nevertheless, the energy dependence detected in the present data set is enough to obtain the local structural information around Co.

3. Structural analysis

Since the intensity pattern of the Y-phase measured by Mo Kα radiation indicated no significant change from that of the reported $Al_{12.1}(Co_{0.88}Ni_{0.12})_4$ [14], space group symmetry of $C2/m$ (No.12) was selected for further analysis. Starting from the initial structural parameters of $Al_{12.1}(Co_{0.88}Ni_{0.12})_4$, several iteration of least-squares calculation allowed to assign the 10 independent sites as two heavy metal sites (Co(1) and Co(2)), six light metal sites (Al(1), Al(2), Al(3), Al(4), Al(5) and Al(7)) and two remaining geometrically disordered sites (Al(61) and Al(62)). The local structure around the disordered site of Al(62) indicates the short distance Al(62)-Al(2) = 2.394(3) Å, which appears not to be common distance for Al–Al pairs.

Since the AXS method is well described in many literatures [13,15,16], we describe only the specific details for the present AXS analysis. When the intensities were measured at two energies 7.685 keV and 7.560 keV in the close vicinity of the absorption edge of Co the detected variation in structural factors with energy is attributed to only the anomalous scattering terms of Co, because the anomalous dispersion effects arising from the other element appear to be insignificant in this energy region. Therefore, the distribution

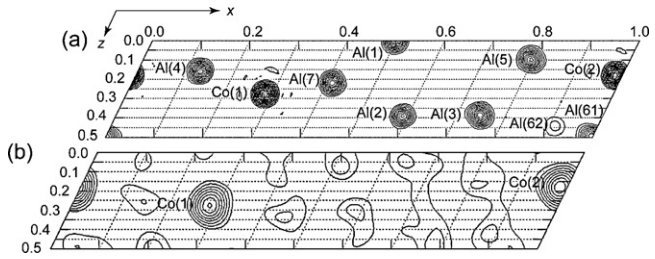

Fig. 1. (a) Electron density map ($y = 0$) obtained by ordinary single crystal X-ray diffraction. The contours are at an interval of 5 electron/Å^3. (b) The distribution map of Co ($y = 0$) analyzed by the AXS measurement at Co K absorption edge. The contours are drawn at an interval of 0.6 electron/Å^3.

map of Co; $\rho_{Co}(x,y,z)$ can be obtained by the Fourier transformation as follows,

$$\rho_{Co}(x,y,z) = \frac{1}{V}\sum_h\sum_k\sum_l \left\{ \left|F_{hkl,150eV}\right| \exp(i\alpha_{hkl,7.560keV}) - |F_{hkl,25eV}| \exp(i\alpha_{hkl,7.685keV}) \right\} \times \exp[-2\pi i(hx + ky + lz)], \quad (1)$$

where V is the volume of a unit cell, $|F_{h\,k\,l,E\,keV}|$ and $\exp(i\alpha_{h\,k\,l,E\,keV})$ are the structural factor in the absolute unit and the phase term for a h, k, l reflection measured at the energy E keV, respectively. Since phase terms $\exp(i\alpha_{h\,k\,l,7.560\,keV})$ and $\exp(i\alpha_{h\,k\,l,7.685\,keV})$ can be approximated by 1 or −1 on the basis of the ordinary single crystal X-ray diffraction by using Mo Kα radiation, $\rho_{Co}(x,y,z)$ can be readily obtained as shown in Fig. 1. It should be noted that the measured structural factors at two energies below the Co K absorption edge, were scaled into an absolute unit by using the structural parameters obtained in the ordinary analysis.

The information on $\rho_{Co}(x,y,z)$ obtained by the present AXS analysis indicates the distribution of Co at the Co(1) and Co(2) sites only and subsequently excludes that at the other sites. This useful information confirmed the structural model and atomic coordinates and corresponding thermal parameters were safely refined by using the data set measured by the Mo Kα radiation. Inter-atomic distance of Al(61)-Al(62) = 1.338(5) Å suggested the alternative occupation for this paired sites and the summation of the converged occupations for Al(61) and Al(62) was almost equal to a unity. Then, a reasonable restriction so as to keep them to be a unity in total was employed. Introducing anisotropic temperature factors and an extinction parameters of the SHELXL software ($\chi = 0.0036(4)$), the present refinement finally converged to $R(F) = 0.0288$ for the observed 953 reflections. The final structural parameters are listed in Table 2. The chemical composition for the converged structural model was $Al_{24.42(2)}Co_8$, which corresponds well with that determined by EPMA. It may be added that the Al(62) site with a relatively low occupation of Al was refined isotropically.

Table 2.1
Atomic coordinates and equivalent displacement parameters for Y-$Al_{13-x}Co_4$ ($x = 0.8$).

Site	Occupancy	x	y	z	U_{eq}
Co(1)	1.0	0.28553(2)	0	0.28056(6)	0.00691(10)
Co(2)	1.0	0.98820(3)	0	0.18168(6)	0.00775(10)
Al(1)	1.0	1/2	0	0	0.0082(2)
Al(2)	1.0	0.59058(7)	0	0.3950(2)	0.0214(3)
Al(3)	1.0	0.25057(7)	0	0.6073(2)	0.0129(2)
Al(4)	1.0	0.12869(6)	0	0.1603(1)	0.0100(2)
Al(5)	1.0	0.79884(8)	0	0.0996(2)	0.0147(2)
Al(61)	0.794(5)	0	0	1/2	0.0206(5)
Al(62)	0.206	0.9140(3)	0	0.4456(7)	0.0100(12)*
Al(7)	1.0	0.41332(6)	0	0.2228(1)	0.0094(2)

* The temperature factor for the Al(62) site was refined isotropically.