Determination of the chiral structure of $CsCuCl_3$ using anomalous x-ray scattering near the Cs K absorption edge

Determination of the chiral structure of CsCuCl$_3$ using anomalous x-ray scattering near the Cs K absorption edge

T Koiso†, K Yamamoto†, Y Hata†, Y Takahashi†, E Kita†, K Ohshima† and F P Okamura‡

† Institute of Applied Physics, University of Tsukuba, Tsukuba 305, Japan
‡ National Institute for Research in Inorganic Materials, Tsukuba 305, Japan

Abstract. A structural study of CsCuCl$_3$, grown from aqueous solution, was performed using anomalous x-ray scattering near the Cs K absorption edge to determine an absolute configuration of constituent atoms. The sense of the helical structure of the CuCl$_3$ chain was found to be predominantly right-handed through a comparison of observed Bragg Bijvoet ratios with calculated ones. Assuming that CsCuCl$_3$ consists of the two domains (i.e. right- and left-handed helices), we estimate that the volume fraction for the right-handed helix is 0.87 ± 0.02.

1. Introduction

Caesium cupric chloride, CsCuCl$_3$, possesses the hexagonal CsNiCl$_3$-type ($P6_3/mmc$) structure (Achiwa 1969, Melamud *et al* 1974) above the transition temperature T_c (423 K) and is distorted to low symmetry by a cooperative Jahn–Teller effect below T_c (Kroese *et al* 1971, Hirotsu 1975, 1977, Lee 1979). At T_c, all of the constituent atoms are displaced from the normal position along the c-axis to form a helix whose period is three times the lattice constant C of the high-temperature phase. The space group of the low-temperature phase belongs to the $P6_122$ group for right-handed helices of the CuCl$_3$ chain, or the $P6_522$ group for left-handed ones (Wells 1947, Schlueter *et al* 1966); these have an enantiamorphous relation with each other. As far as we are aware, CsCuCl$_3$ is a unique screw antiferroelectric crystal. A priority of chirality probably exists in CsCuCl$_3$. In addition, CsCuCl$_3$ has a peculiar magnetic property: the predominant magnetic interaction in CsCuCl$_3$ is a ferromagnetic intrachain interaction. But the lack of inversion symmetry at the Cu^{2+} site produces an antisymmetric interaction (the Dzyaloshinsky–Moriya interaction), resulting in a helical spin structure along the c-axis with a rotation angle of 5.1° (Adachi *et al* 1980, Mekata *et al* 1995). In addition to the intrachain interaction, an antiferromagnetic interchain interaction gives rise to a 120° structure in the c-plane of a triangular lattice. As a consequence, a double-helix magnetic structure is formed. To examine the correlation between the sense of spin rotation and that of crystal rotation, it is important first to determine the handedness of the crystalline helix in a single crystal of CsCuCl$_3$.

Sano *et al* (1986) reported that as-grown crystals of CsCuCl$_3$ grown from aqueous solution were predominantly dextrorotatory on the basis of a measurement of optical rotatory power. However, they did not determine the absolute structure of CsCuCl$_3$. Anomalous scattering provides a key to solving such structures by x-ray diffraction, because the real and imaginary parts of the dispersion correction in an atomic scattering factor contribute

to an enhancement of the difference for the scattered intensities. In fact, α-quartz crystal, which has optical laevorotatory power, was proved to belong to the $P3_12$ group of the right-handed helix by use of x-ray anomalous scattering (de Vries 1958, Chandraseckhar 1960, Zachariasen 1965). It is, therefore, interesting to perform a structural study of CsCuCl$_3$ by this technique.

We describe the theoretical background for determining the absolute structure of non-centrosymmetric crystals, such as CsCuCl$_3$, via x-ray anomalous scattering in the following section. There are two K absorption edges of CsCuCl$_3$: 35.968 keV for Cs and 8.984 keV for Cu. Using an x-ray energy near the Cs K absorption edge for the intensity measurements at all desired Bragg reflections is advantageous because it allows the use of transmission geometry as compared with the x-ray intensity measurements near the Cu K absorption edge. In the present work, we determine the absolute configuration of constituent atoms in CsCuCl$_3$ at room temperature by measuring Bragg intensities near the Cs K absorption edge.

2. Theory

In this section, a theoretical procedure is described for determining the structure of a non-centrosymmetric crystal, such as CsCuCl$_3$ by x-ray anomalous scattering. The structure factor $F^{R(L)}(hkl)$ of the right-handed helix of the CuCl$_3$ chain (or the left-handed one) in CsCuCl$_3$ is given by

$$F^{R(L)}(hkl) = \sum_m (f_m^0 + f_m' + \mathrm{i}f_m'') \exp(2\pi \mathrm{i}\boldsymbol{h} \cdot \boldsymbol{r}_m^{R(L)}) \exp(-B_m s^2) \tag{1}$$

where the summation over m runs over all atoms positioned at $\boldsymbol{r}_m^{R(L)}$ in the unit cell. f_m^0 is the atomic scattering factor found in the *International Tables for Crystallography* (1992), and f_m' and f_m'' are the real and imaginary parts of the dispersion correction (Sasaki 1989). B_m, $\boldsymbol{h}$ and s are the temperature factor of the mth ion, the reciprocal-lattice vector and $\sin\theta/\lambda$, respectively, and θ is the diffraction angle and λ is the wavelength of the x-ray. When we can disregard the influence of the anomalous dispersion term at Cu and Cl sites, equation (1) is rewritten as

$$F^{R(L)}(hkl) = F^0(hkl) + \sum_n^6 (f_{Cs}' + \mathrm{i}f_{Cs}'') \exp(2\pi \mathrm{i}\boldsymbol{h} \cdot \boldsymbol{r}_n^{R(L)}) \exp(-B_{Cs} s^2) \tag{2}$$

where $F^0(hkl)$ is the normal structure factor, including the temperature factor, and B_{Cs} is the temperature factor of the Cs$^+$ ion.

If the structure of CsCuCl$_3$ used in experiments consists of a mixture of two domains with right-handed and left-handed helices, the observed intensity $I_{obs}(hkl)$ is given by

$$I_{obs}(hkl) = \alpha \left| F^R(hkl) \right|^2 + (1-\alpha) \left| F^R(hkl) \right|^2 = \alpha I^R(hkl) + (1-\alpha) I^L(hkl) \tag{3}$$

where α is a volume fraction and $I^R(hkl)$ ($I^L(hkl)$) is the intensity of the 100% right-handed helix (the 100% left-handed helix). Equation (3) can be transformed using the following equation:

$$I^L(hkl) = I^R(\bar{h}\bar{k}\bar{l}) \tag{4}$$

in which case equation (3) becomes

$$I_{obs}(hkl) = \alpha I^R(hkl) + (1-\alpha) I^R(\bar{h}\bar{k}\bar{l}). \tag{5}$$

Similarly, the following relation is obtained:

$$I_{obs}(\bar{h}\bar{k}\bar{l}) = \alpha I^R(\bar{h}\bar{k}\bar{l}) + (1 - \alpha)I^R(hkl). \tag{6}$$

From equations (5) and (6), a volume fraction α is determined:

$$\alpha = \frac{R_{obs}(hkl)R^R(hkl) - 1}{(R_{obs}(hkl) + 1)(R^R(hkl) - 1)} \tag{7}$$

where

$$R^R(hkl) = \frac{I^R(hkl)}{I^R(\bar{h}\,\bar{k}\,\bar{l})} \tag{8}$$

and

$$R_{obs}(hkl) = \frac{I_{obs}(hkl)}{I_{obs}(\bar{h}\,\bar{k}\,\bar{l})}. \tag{9}$$

The calculated ratios $R^R(hkl)$ can be determined from the intensity of the 100% right-handed helix.

3. Experimental details

Anomalous scattering measurements were carried out by use of an analytical system, designed to obtain electron density distributions by diffraction of ultrashort-wavelength photons, at the National Institute for Research in Inorganic Materials (NIRIM), Science and Technology Agency of Japan, manufactured by Rigaku Denki Co., Japan. One of its salient features is the capability of exciting x-rays with much higher energies (i.e. ultrashort wavelength) in comparison with conventional x-ray wavelength generators hitherto in use. The maximum input of the x-ray generator in the system is 2 kW and the maximum tube voltage and tube current are 200 keV and 12 mA. Because the x-rays are generated with a demountable rotating anode, the x-ray source is highly stable. In the present experiment, white x-rays from a tungsten (W) target were used and a Ge solid-state detector (SSD) was employed for measuring diffracted spectra from the specimen. The four-circle diffractometer was used to collect three-dimensional intensities. To obtain the calculated intensity of a 100% right-handed helix $I_{cal}^R(hkl)$ or that of a 100% left-handed helix $I_{cal}^L(hkl)$, the structural parameters were determined by an ordinary structure analysis using the Ag Kα wavelength far from the Cs K absorption.

Single crystals of CsCuCl₃ were grown by isothermal evaporation of an aqueous solution containing CuCl₂ and CsCl. Excess CuCl₂, nearly 10% from the stoichiometric composition, was used to prevent formation of Cs₂CuCl₄. The crystal obtained is a dark, red-brown, hexagonal bipyramid with $\{10\bar{1}1\}$ faces. A single crystal for measuring the scattering intensities was rounded to a sphere to prevent the need for complex absorption correction.

4. Results and analysis

In the measurements of anomalous scattering, we have chosen an x-ray energy of 39 keV, as the energy of the Cs K absorption edge is 35.968 keV. For reference, the calculated values of the anomalous dispersion curves, f' and f'', for a Cs atom are shown in figure 1 (Sasaki 1989). An example of the diffraction spectra at a fixed angle is shown in figure 2. In addition to Cs Kα and Kβ fluorescences from the specimen and W Kα and Kβ characteristic lines from the target, (2, 1, 10) and (4, 2, 20) Bragg reflections are obtained. We can select the characteristic Bragg reflections with the use of the four-circle diffractometer. Figure 3
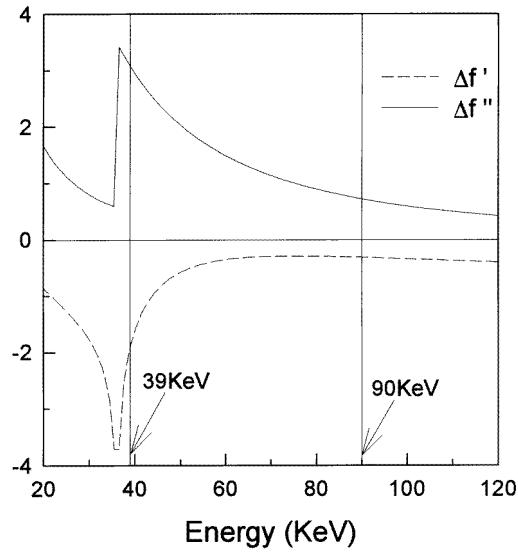
Figure 1. The real and imaginary parts of the dispersion correction in the atomic scattering factors, f' and f'', for a Cs atom versus energy. The two energies at 39 keV and 90 keV were used in the present measurement.
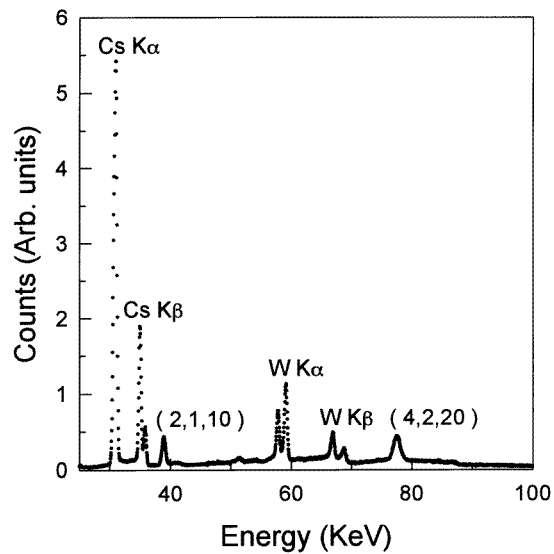

Figure 2. The diffraction spectrum from a $CsCuCl_3$ single crystal versus energy. Anomalous dispersion strongly influences the intensity for the (2,1,10) reflection. Both Cs Kα and Kβ fluorescences from the specimen and W Kα and Kβ characteristic lines from the target are also obvious.

shows the results for (212) and ($\bar{2}\bar{1}\bar{2}$) reflections thus measured. It is obvious that there is a noticeable difference between (212) and ($\bar{2}\bar{1}\bar{2}$) reflections.

To ascertain that the influence of anomalous dispersion becomes smaller when the energy
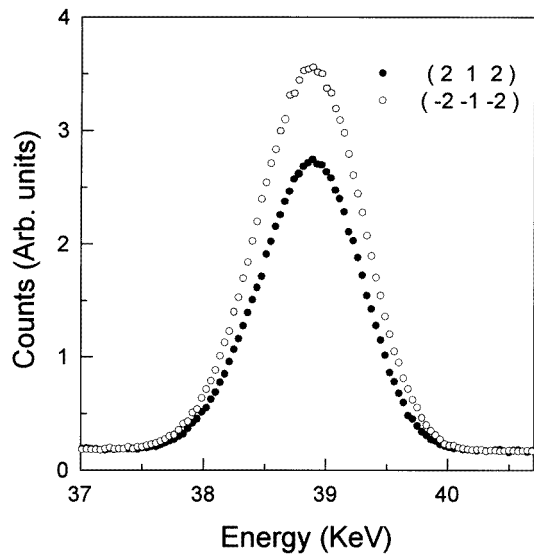
Figure 3. A comparison of (212) and $(\bar{2}\bar{1}\bar{2})$ reflections at an x-ray energy of 39 keV, showing the effect of anomalous dispersion.
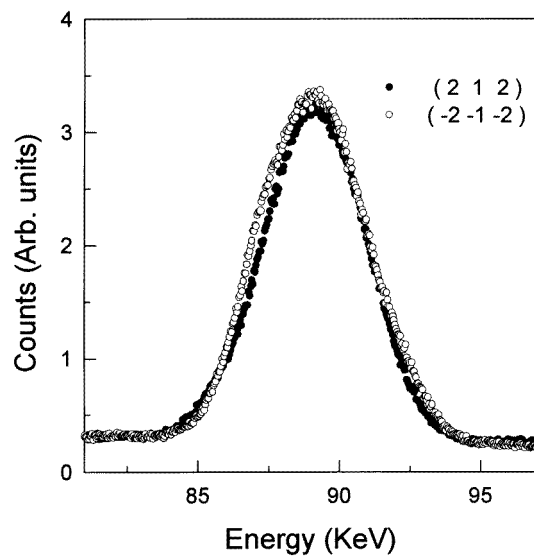

Figure 4. A comparison of (212) and $(\bar{2}\bar{1}\bar{2})$ reflections at an x-ray energy of 90 keV, far from the Cs K absorption edge.

is sufficiently far from the Cs K absorption edge, we have carried out intensity measurements using an x-ray energy of 90 keV. Figure 4 shows the results for (212) and $(\bar{2}\bar{1}\bar{2})$ reflections. As expected, the intensity for the (212) reflection is approaching that for the $(\bar{2}\bar{1}\bar{2})$ reflection. In the same way, we have measured other Friedel-pair reflections, $I_{obs}(hkl)$ and $I_{obs}(\bar{h}\bar{k}\bar{l})$. The intensity ratios between the Friedel-pair reflections, $R_{obs}(hkl)$, were obtained after

Table 1. The values of $R_{obs}(hkl)$, $R_{cal}^R(hkl)$, $R_{cal}^L(hkl)$ and α for hkl reflections. $R_{obs}(hkl)$, $R_{cal}^R(hkl)$ and $R_{cal}^L(hkl)$ are intensity ratios between the Friedel pairs as observed and as calculated for 100% right-handed and left-handed helices, respectively. α is the volume fraction of the region for a right-handed helix. The average value of α is also shown.

h	k	l	R_{obs}	$R_{cal}^R(hkl)$ $P6_122$	$R_{cal}^L(hkl)$ $P6_522$	α
2	1	2	0.736	0.664	1.51	0.88
2	1	10	1.83	2.12	0.472	0.91
3	2	2	0.858	0.774	1.29	0.80
3	2	14	0.693	0.621	1.61	0.89
4	2	1	0.913	0.884	1.13	0.87
				$\alpha = 0.87 \pm 0.02$		

summing up six equivalent reflections. They are shown in table 1 for (212), (2, 1, 10), (322), (3, 2, 14), and (421). In these measurements, the Friedel-pair reflections were chosen as follows: (1) the members of the pair should differ greatly from each other; and (2) the index of the pair should be as different as possible from the others.

Next, we must calculate the intensity ratio $R^R(hkl)$ in equation (8) at 39 keV to obtain the volume fraction α. The integrated intensities of $CsCuCl_3$ were measured at a wavelength far from the Cs K absorption edge, i.e. at the Ag Kα characteristic line, with the use of a conventional four-circle diffractometer. In the measurement, Friedel-pair reflections whose structure factors differed by more than 0.5% were deleted in determining the structural parameters. We then obtained the intensity ratios for a 100% right-handed helix, or a 100% left-handed helix, R_{cal}^R or R_{cal}^L, by calculating the intensities at 39 keV with the use of such structural parameters. These values are shown in table 1 in which $R_{cal}^{R(L)}$ was obtained from the following equations:

$$R_{cal}^{R(L)}(hkl) = \frac{I_{cal}^{R(L)}(hkl)}{I_{cal}^{R(L)}(\bar{h}\bar{k}\bar{l})}. \tag{10}$$

It is reasonable to replace $R^R(hkl)$ by $R_{cal}^R(hkl)$ in equation (7). α-values for the five reflections thus obtained are tabulated in table 1. The average value of the five is given as

$$\alpha = 0.87 \pm 0.02.$$

5. Summary

In this report, we have measured Bragg intensities to determine the volume fraction for the right-handed helix in $CsCuCl_3$, using high-energy x-rays. We have found different intensities between various Friedel-pair reflections near the Cs K absorption edge (39 keV). Such differences were smaller between various Friedel-pair reflections obtained using 90 keV x-rays, sufficiently far from the Cs K absorption edge. If the $CsCuCl_3$ crystal consists of two domains (i.e. right- and left-handed helices) and our procedure in the preceding section is correct, then the α-value obtained is 0.87 ± 0.02. We conclude that single crystals of $CsCuCl_3$ grown from aqueous solution consist mainly of a right-handed helix of the $CuCl_3$ chain for the present sample. As a further study, it will be necessary to perform a polarized neutron diffraction experiment to determine the correlation between the sense of spin rotation and that of crystal rotation in single crystals of $CsCuCl_3$. We are also planning to perform measurements of the optical rotation in the same crystal.

Acknowledgments

References

Achiwa N 1969 *J. Phys. Soc. Japan* **27** 561
Adachi K, Achiwa N and Mekata M 1980 *J. Phys. Soc. Japan* **49** 545
Chandraseckhar S 1960 *Proc. R. Soc.* A **259** 3479
de Vries A 1958 *Nature* **181** 1193
Hirotsu S 1975 *J. Phys. C: Solid State Phys.* **8** L12
——1977 *J. Phys. C: Solid State Phys.* **10** 967
International Tables for Crystallography 1992 vol C (Dordrecht: Kluwer–Academic)
Kroese C J, Tindemans-van Eyndhoven J C M and Maaskant W J A 1971 *Solid State Commun.* **9** 1707
Lee B S 1979 *J. Phys. C: Solid State Phys.* **12** 855
Mekata M, Ajiro Y, Sugino T, Oohara A, Ohara K, Yasuda S, Oohara Y and Yosizawa H 1995 *J. Magn. Magn. Mater.* **140–144** 1987
Melamud M, Pinto H, Makovsky J and Shaked H 1974 *Phys. Status Solidi* b **63** 699
Sano M, Iio K and Nagata K 1986 *Japan. J. Appl. Phys.* **25** 627
Sasaki S 1989 *KEK Report* 88-14
Schlueter A W, Jacobson R A and Rundle R E 1966 *Inorg. Chem.* **5** 277
Wells A F 1947 *J. Chem. Soc.* **1947** 1662
Zachariasen W H 1965 *Acta Crystallogr.* **18** 714