

Thermal-Vibration Effect on X-ray Integrated Intensities Near the Copper *K* Absorption Edge in CuI: Determination of the Temperature Factors

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(Received 21 April 1980; accepted 28 July 1980)

Abstract

The energy dependence of the integrated intensities $I_h(\omega)$ and $I_k(\omega)$ and of their ratio $r_h(\omega)$, around an absorption edge, are greatly affected by thermal vibrations of atoms. This has been experimentally shown by the present energy-dispersive diffractometry for a mosaic crystal of CuI, for which thermal vibrations are especially large even at room temperature. The temperature factor values $B_{\text{Cu}} = 3.3 \pm 0.1$ and $B_{\text{I}} = 2.0 \pm 0.1 \text{ \AA}^2$ have been determined in the following way: the $f''_{\text{Cu}}(\omega)$ curve has been determined from the absorption curve, and therefrom the $f'_{\text{Cu}}(\omega)$ curve has been calculated by the dispersion relation. By the use of these curves, the intensity curves $I_{555}(\omega)$ and $I_{555}(\omega)$ were obtained, and then the temperature factors were determined by finding the best fit between the above $I(\omega)$ curves and the observed one. Also, the experimental fine structure of the Friedel ratio $r_3(\omega)$ is shown as a function of energy and compared with the calculated values.

Introduction

As is well known, X-ray anomalous scattering techniques are commonly used for investigating the absolute polarity sense of non-centrosymmetric crystals. The crystallographic polarity of CuBr and CuCl was established by Monier & Kern (1955) at the Cu *K* edge, and for CuI by Bhalla & White (1971) at the I *K* edge.

Although the polarity of CuI has been determined, the result was not related either to the etch pattern or to

the piezoelectric test, so that the positive [111] direction was not given in the absolute sense. The opposite faces (111) and ($\bar{1}\bar{1}\bar{1}$) behave differently with regard to oxidation (Lavine, Rosenberg & Gatos, 1958) and etching (Maringer, 1958). Then Bhalla & White (1971) confirmed that, if the direction from Cu at (0,0,0) to I at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ is defined as [111], the (111) plane contains Cu^+ ions while the ($\bar{1}\bar{1}\bar{1}$) contains I^- ions.

The signs of the piezoelectric coefficients of the copper halide crystals have been determined (Miller, Abrahams, Barns, Bernstein & Nordland, 1971) and we now use the generally accepted convention that a positive [111] direction in the zinc blende structure points from the metal Cu^+ ion to the nearest anion plane (Turner, Kaminow & Schwab, 1974); according to this convention, the measurement of the sign of the piezoelectric effect showed that the Cu face becomes positive on a uniaxial extension (Miller *et al.*, 1971).

Besides the polarity problem, many semiconductors of zinc blende structure, cuprous halides and silver iodide, show various anomalous properties. According to Miyake & Hoshino (1958), cuprous halides show anomalous behaviour, both in the temperature factor of the Cu atoms and in ionic property, as the temperature increases. From X-ray and calorimetric measurements, they proved that the thermal vibrations of copper atoms were anomalously enhanced as the temperature increased; then Matsubara (1975) showed that the phase transition of CuI can be explained in terms of an anisotropic anharmonic thermal vibration of Cu atoms. The origin of this large amplitude of thermal vibration of Cu atoms at room temperature can be understood in terms of the shallow anisotropic potential of Cu atoms which is typical in cuprous halides of the zinc blende type. This anomalous increase in thermal displacement of copper atoms is related to the ionic conductivity due to metallic ions.

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Owing to these large thermal vibrations in CuI, this crystal is particularly suitable for testing the effect of the thermal vibration on the X-ray integrated intensity variation around an absorption edge. In a previous paper (Morlon, Fukamachi & Hosoya, 1979), it has been shown that the Bragg reflexion intensity generally shows a large change in the energy region near the absorption edge of a constituent atom, and that this effect depends largely upon the value of the thermal parameters B_j in both perfect and mosaic cases. Consequently, the Friedel-pair intensity ratio is also affected and the B_j values must be taken into account when this ratio is calculated near the absorption edge.

In the present work, an experimental study is reported on the integrated intensities for a pair of opposite reflexions from a mosaic CuI crystal by energy-dispersive diffractometry. In order to calculate the energy dependence of the integrated intensities, anomalous scattering factors $f''_{\text{Cu}}(\omega)$ and $f'_{\text{Cu}}(\omega)$ have been determined in the energy region very close to the Cu K edge. Then the experimental and the calculated intensities were compared, and the energy dependence of the Friedel-pair ratio is given for the experimental and the calculated cases.

Experimental

The present experimental work consists of two different measurements on CuI, both in an energy range near the Cu K absorption edge: the determination of the linear absorption coefficient $\mu(\omega)$ and the intensity measurements of the 555 and $\bar{5}\bar{5}\bar{5}$ reflexions.

The experimental set-up consists of a two-circle goniometer (Fig. 1) and a data processing unit (Fig. 2). The crystal in Fig. 1 is either a Si crystal used as a monochromator for the absorption measurement, or the CuI crystal for the measurements of integrated intensities. The Mo target tube, operated at 30 kV and 30 mA, was rotated instead of the Ge(Li) detector with

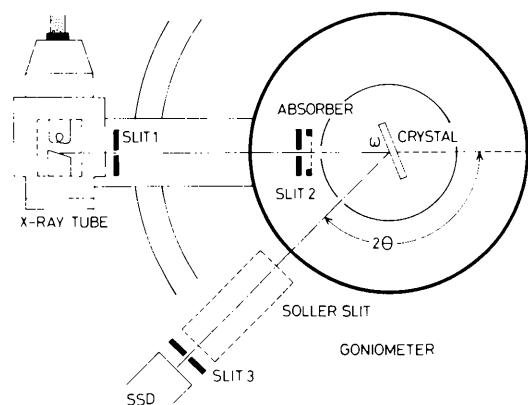


Fig. 1. Experimental set-up for the absorption and integrated intensity measurements.

a heavy Dewar. The energy resolution $\Delta\omega$ was about 1 eV when the 444 Si reflexion was brought near the Cu K edge ($\omega_K = 8980$ eV) at $2\theta = 123.35^\circ$, and the measured energy range in eV was

$$\omega_K - 20 < \omega < \omega_K + 40$$

and the energy step was 2.1 eV.

Owing to the heavy absorption due to I atoms in CuI, the sample should be thinner than 10 μm ; such a thickness could not be attained in a brittle crystal. Therefore, a powdered sample sandwiched between adhesive tapes was used as a uniform film protected from moisture, although CuI is less sensitive to humidity than CuCl and CuBr.

In the second part of the experiment, the integrated intensities of the 555 and $\bar{5}\bar{5}\bar{5}$ reflexions in the symmetrical Bragg case were measured on a CuI crystal plate. The energy resolution was 1 eV at $2\theta = 163.25^\circ$ which corresponds to the Cu K edge.

In order to obtain clean surfaces and also to avoid a non-essential effect due to some difference in surface state of the two sides, the CuI crystal was chemically cleaned with nitric acid after being mechanically polished. This acid proved not to differentiate (111) from ($\bar{1}\bar{1}\bar{1}$) for CuI, although it acts as a differential etchant for CuCl and CuBr (Monier & Kern, 1955). In fact, even if an asymmetry effect still remains after etching, it can be easily dropped using even $\pm hhh$ reflexions; these reflexions do not have the polarity effect, and their experimental intensities can be used to scale the 555 and $\bar{5}\bar{5}\bar{5}$ intensities, thus eliminating surface effects.

Measurement of $f''(\omega)$ and calculation of $f'(\omega)$

In order to obtain the linear absorption coefficient $\mu(\omega)$ for a powdered sample, the thickness has to be determined by indirect methods. The data processing system enables us to collect simultaneously the intensities of all hhh reflexions from Si. The scattering angle is chosen so that the 444 reflexion occurs at energies very near the Cu K edge (ω_K); it follows that other hhh

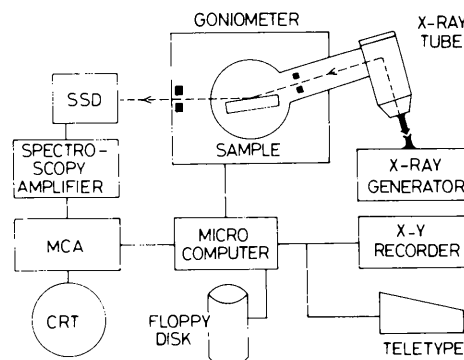


Fig. 2. Schematic diagram of the SSD diffractometer system used.

reflexions correspond to energies very far from any absorption edge; then a comparison between the experimental absorption data at several energies and those calculated from the empirical relation of Victoreen (1962) give the sample thickness. In addition, corrections were made for non-uniform thickness, perforations (Hunter, 1977) and porosity; the sample thickness was equivalent to a bulk sample 8.5 μm thick.

The general methods of determining the imaginary part $f''(\omega)$ from the linear absorption coefficient $\mu(\omega)$ were reported in detail by Fukamachi & Hosoya (1975) and Fukamachi, Hosoya, Kawamura & Okunuki (1977). Outlined here are the main relations used in the calculation of $f''(\omega)$ from experimental data $\mu(\omega)$.

The zero Fourier component $\chi''_0(\omega)$ of the electron polarizability, the imaginary part of the atomic scattering factor $f''_j(\omega)$ of an atom j , and the linear absorption $\mu(\omega)$ are all related by the following relations:

$$\mu(\omega) = -\frac{\omega}{c} \chi''_0(\omega) \quad (1)$$

and

$$\chi''_0(\omega) = -\frac{1}{v} \frac{4\pi}{\omega^2} \sum f''_j(\omega) \quad (2)$$

where atomic units are used, c is the velocity of light, v is the volume of a unit cell and the summation is taken over a unit cell.

In the case of the zinc blende CuX crystal, we obtain the final relation

$$f''_{\text{Cu}}(\omega) + f''_{\text{X}} = 3.578 \times 10^{-8} a^3 \omega \mu(\omega) \quad (3)$$

where a is the unit-cell parameter in \AA , ω is in eV and μ is in mm^{-1} .

Relation (3) enables us to determine $f''_{\text{Cu}}(\omega)$, as f''_{X} has constant values near the Cu K edge. The real part $f'_K(\omega)$ of a K electron was calculated from the measured values of the imaginary part $f''_K(\omega)$ using the dispersion relation (Sakurai, 1967; Fukamachi, Hosoya, Kawamura & Okunuki, 1977; Kawamura & Fukamachi, 1978),

$$f'_K(\omega) = \frac{2}{\pi} \int_{\omega_K}^{\infty} \frac{\omega' f''_K(\omega')}{\omega^2 - \omega'^2} d\omega'. \quad (4)$$

In this formula, outside the measured energy range, $f''_K(\omega)$ is assumed to be given by an empirical formula:

$$f''_K(\omega) = (\pi/2)(\omega_K/\omega)^q K^{-1}(q_K - 1)g_K \quad \text{for } \omega > \omega_K \quad (5)$$

and

$$f''_K(\omega) = 0 \quad \text{for } \omega < \omega_K. \quad (6)$$

In (5), g_K is the oscillator strength at the energy edge and the numerical values for g_K and q_K are from Cromer (1965).

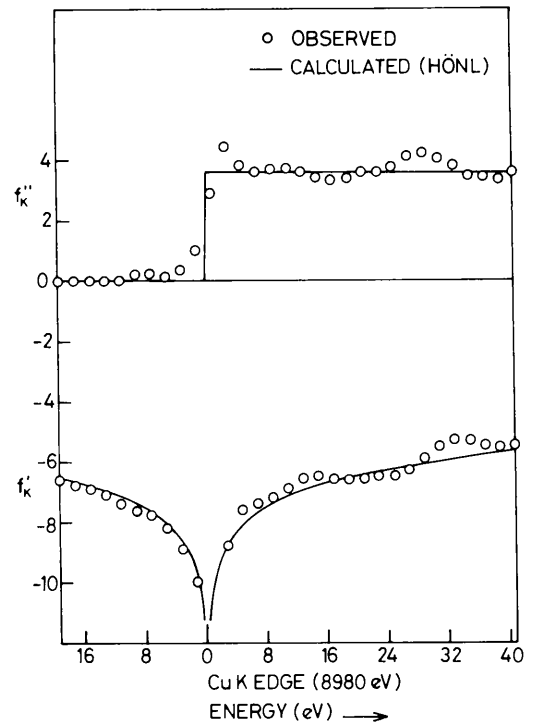


Fig. 3. Anomalous scattering factors $f'_{\text{Cu}}(\omega)$ and $f''_{\text{Cu}}(\omega)$ in CuI near the Cu K edge. [Circles are measured values and solid lines are calculated values from Hönl's (1933) relation.]

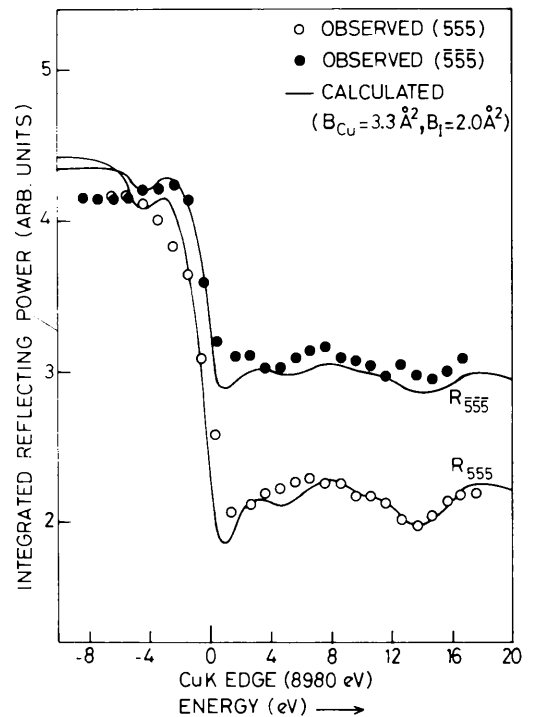


Fig. 4. Comparison between the calculated and the measured integrated reflecting power $R_{555}(\omega)$ and $R_{555}(\omega)$. The best fit is obtained for $B_{\text{Cu}} = 3.3 \text{ \AA}^2$, $B_{\text{I}} = 2.0 \text{ \AA}^2$.

The fine structure of $f''_{Cu}(\omega)$ and $f'_{Cu}(\omega)$ of *K* electrons is shown in Fig. 3 together with the values calculated by Hönl's (1933) relations.

Measurement and calculation of the integrated reflexion intensities near the Cu *K* edge

The integrated intensities of the 555 and $\bar{5}\bar{5}\bar{5}$ reflexions from CuI have been measured under the above experimental conditions. The energy dependence of integrated reflexion powers R_{555} and $R_{\bar{5}\bar{5}\bar{5}}$ is shown in Fig. 4, where the fine structure above the Cu *K* edge is clearly seen.

The main purpose of the present measurements is to look at the effect of the thermal vibrations on the integrated intensities around the absorption edge. In order to carry out a quantitative analysis, the theoretical integrated reflecting power has been calculated for the mosaic case.

For a symmetric Bragg reflexion, the integrated reflecting power R_h for a mosaic crystal in the energy-dispersive mode is given by

$$R_h = Q_h / |2\mu(\omega_B)| \tag{7}$$

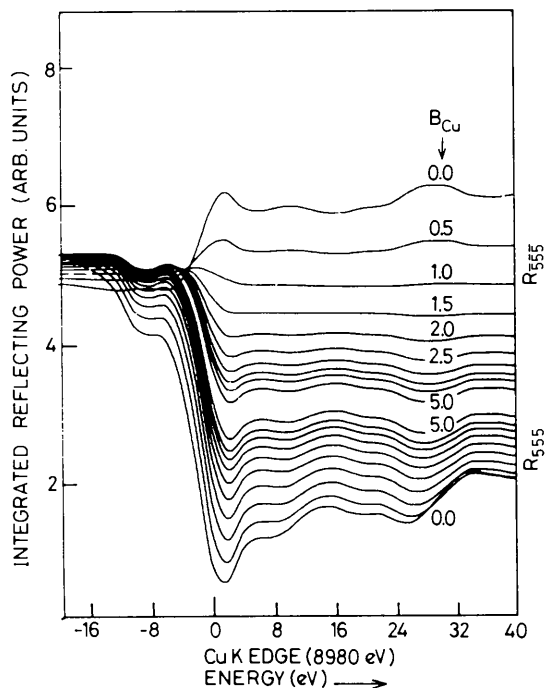


Fig. 5. Calculated curves for the energy dependence of the integrated reflecting powers $R_{555}(\omega)$ and $R_{\bar{5}\bar{5}\bar{5}}(\omega)$ for CuI near the Cu *K* edge, taking account of the measured values $f'_{Cu}(\omega)$ and $f''_{Cu}(\omega)$. The following temperature factors are used: $B_{Cu} = 0.0$ to 5.0 and $B_1 = 2.0 \text{ \AA}^2$.

Table 1. Numerical values used for anomalous and atomic scattering factors and other quantities

f'_{Cu}, f''_{Cu} : experimental data; f'_1, f''_1 : calculated values from Parratt & Hempstead (1954).

The atomic scattering factors for the 555 reflexion are $f_{Cu}^0 = 9.66$ and $f_1^0 = 21.90$.

The lattice constant of CuI = 6.0427 \AA .

ω (eV)	f'_{Cu}	f''_{Cu}	f'_1	f''_1
8960	-6.62	0.50	-1.38	4.65
8962	-6.76	0.50	-1.38	4.65
8964	-6.93	0.50	-1.38	4.65
8966	-7.13	0.50	-1.37	4.65
8968	-7.43	0.54	-1.37	4.64
8970	-7.64	0.72	-1.37	4.64
8972	-7.76	0.76	-1.37	4.64
8974	-8.22	0.66	-1.37	4.64
8976	-8.89	0.85	-1.37	4.64
8978	-9.95	1.53	-1.37	4.64
8980	-10.20	3.41	-1.37	4.64
8982	-8.77	4.90	-1.37	4.63
8984	-7.57	4.34	-1.37	4.63
8986	-7.39	4.09	-1.37	4.63
8988	-7.25	4.18	-1.37	4.63
8990	-6.91	4.24	-1.37	4.63
8992	-6.62	4.09	-1.37	4.63
8994	-6.53	3.89	-1.37	4.63
8996	-6.59	3.81	-1.36	4.62
8998	-6.67	3.92	-1.36	4.62
9000	-6.59	4.07	-1.36	4.62
9002	-6.49	4.11	-1.36	4.62
9004	-6.54	4.27	-1.36	4.62
9006	-6.34	4.60	-1.36	4.62
9008	-5.89	4.73	-1.36	4.61
9010	-5.52	4.57	-1.36	4.61
9012	-5.30	4.30	-1.36	4.61
9014	-5.35	4.00	-1.36	4.61
9016	-5.46	3.97	-1.36	4.61
9018	-5.50	3.99	-1.36	4.61
9020	-5.45	4.09	-1.36	4.61

where

$$Q_h = (2\pi c)^3 r_e^2 p(\theta_B) |F_h|^2 / (2v^2 \omega_B^2 \sin^2 \theta_B) \tag{8}^*$$

and the remaining notation is given in the previous paper (Morlon *et al.*, 1979). The numerical calculations were carried out with the experimental and theoretical values of the scattering factors shown in Table 1 and the thermal parameters $B_1 = 2.0$ and $B_{Cu} = 0.0$ to 5.0 \AA^2 . The calculated curves for $R_{555}(\omega)$ and $R_{\bar{5}\bar{5}\bar{5}}(\omega)$ show fine structure above the edge (Fig. 5).

As was shown previously (Morlon *et al.*, 1979), the integrated intensity variation near the absorption edge largely depends on the thermal vibrations, and in the present paper a comparison is made between the experimental intensity curves and the calculated ones.

The best fitting between observed and calculated curves has been found when $B_{Cu} = 3.3 \pm 0.1$ and $B_1 = 2.0 \pm 0.1 \text{ \AA}^2$ (Fig. 4). This B_{Cu} value is of the same

* This formula is correct; the power 2 should be added to ω_B in formula (16) in Fukamachi, Hosoya & Okunuki (1976) and formula (15) in Morlon, Fukamachi & Hosoya (1979).

order as the value given by Miyake & Hoshino (1958). According to these authors, both values of B_I and B_{Cu} at room temperature were about 2.0 \AA^2 , but the behaviour of B_I and B_{Cu} were found to be different; B_I increases slowly and linearly with temperature, while B_{Cu} increases anomalously rapidly and becomes larger than 20.0 \AA^2 at 670 K.

Also, the energy dependence of the Friedel ratio R_{555}/R_{555} is given in Fig. 6. The agreement between the experimental and the calculated values might seem to be relatively poor. However, the discrepancy may be mainly attributed to uncertainty in absolute energy determination. It is obvious that a small shift in angle of opposite faces can strongly affect the fine structures of their intensity ratio, when R_{555} and $R_{\bar{5}\bar{5}\bar{5}}$ are measured alternately.

Conclusion

The present experimental study has shown that opposite faces (111) and ($\bar{1}\bar{1}\bar{1}$) of a CuI crystal have different energy dependence of X-ray integrated intensity near an absorption edge. This anomalous scattering effect has been used to determine the temperature factor of the metal atom, and could give a method for determining the temperature factors in non-centrosymmetric structures.

The present paper describes the first attempt to determine the temperature factors of a mosaic crystal, consisting of two kinds of atoms, from the integrated reflexion intensities near the absorption edge. In CuI, this was easily carried out because the B value of Cu is

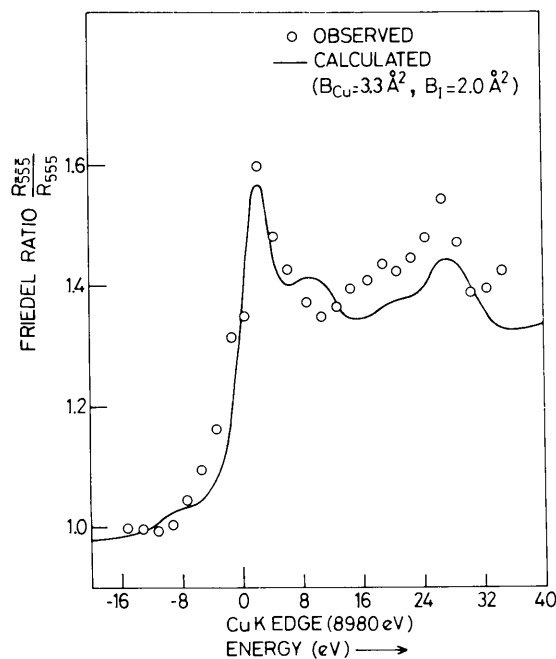


Fig. 6. The energy dependence of the Friedel ratio R_{555}/R_{555} for CuI. For the calculated curves the following thermal parameters are used: $B_{Cu} = 3.3$ and $B_I = 2.0 \text{ \AA}^2$.

large. However, when B is small, the shape of the curve does not change much, and therefore it is not easy to determine the B value.

In the present paper, white X-rays from a conventional tube have been used with the SSD diffractometer. However, if a synchrotron radiation source can be used, more accurate measurements can be carried out on temperature factors by the present technique.

The authors express thanks to Messrs Sakamaki, Koh and Nakano for their help in preparing software and in carrying out the measurements, and to Dr Schwab for supplying them with copper halide crystals. One of the authors (BM) gratefully acknowledges the CNRS-JSPS Scientific Exchange Program, and he is also thankful to Professor Nagai, President of SIT for giving him the opportunity to use the facilities of SIT, and to Professor Godefroy for giving him the opportunity of staying at the Institute for Solid-State Physics, University of Tokyo for several months. The present work has been partly supported by Grant-in-Aid for Scientific Research (project No. 346030) from the Ministry of Education and the Nishina Memorial Foundation.

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