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The electron density distribution in γ -CuBr studied by the maximum-entropy method

K Nakahigashi, J Tamura and H Ishibashi

College of Integrated Arts and Sciences, Osaka Prefecture University, Sakai, Osaka 593, Japan

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Abstract. The electron density distribution of γ -CuBr with sphalerite structure was determined by the maximum-entropy method (MEM) from x-ray powder diffraction data at room temperature. The resultant electron density map was explained in terms of the anharmonic thermal motions and chemical bonding due to hybridized Cu 3d–Br 4p states. The thermal motion of Cu is elongated in the directions of the tetrahedral diagonals. The root mean square displacements of the Cu and Br atoms were 0.220 and 0.156 Å, respectively, and agreed with those determined by the neutron diffraction studies. The observed and calculated (from the MEM density) structure factors are presented.

1. Introduction

CuBr is one of the cuprous halides, which provide attractive systems for the study of anharmonic effects, large thermal motion, structural phase transitions and superionic conductivity. Therefore, many investigators have examined these systems from the experimental and theoretical points of view. Neutron diffraction is one of the powerful methods available for an investigation of anharmonic vibrations. Many studies hitherto reported on CuBr itself and on other cuprous halides. For example, Hoshino *et al* [1] examined a phonon dispersion relation for CuBr in detail via inelastic neutron scattering with a single-crystal triple-axis spectrometer. They found that the phonon energies as well as the shape of the phonon peaks varied considerably with temperature, suggesting that the effect of anharmonicity was remarkable even at room temperature. Harada *et al* [2] investigated the anharmonic effect on the Debye–Waller factors, and the results were interpreted consistently in terms of the Matsubara representation [3]. They also suggested that the anharmonic Debye–Waller factors were closely related to the damping of particular phonons. Recently, Altorfer *et al* [4] examined anharmonic atomic vibrations of γ -CuBr by neutron powder diffraction and determined the temperature factors including the anharmonic effect. They also calculated the nuclear density map of Cu and indicated that the thermal motion of Cu was elongated in the directions of tetrahedral diagonals.

On the other hand, Christensen *et al* [5] calculated the valence charge density distribution of CuBr, together with 33 other compounds, by the relativistic linear muffin-tin-orbital method. The results indicate that the valence bands of CuBr consist of very strongly hybridized Cu 3d and Br 4p states. However, detailed experimental study of the electron density distribution of cuprous halides such as CuBr is still lacking. As is well known, neutron diffraction is usually complementary to x-ray diffraction. In the field of accurate structure analysis, especially from powder data, it is very useful to compare the electron and nuclear densities.

In the present study, we report the electron density distribution for γ -CuBr determined by the maximum-entropy method (MEM) with the aid of x-ray powder diffraction data. The result is compared with neutron diffraction studies and the theoretical electron density distribution.

2. Experimental details

Commercially available CuBr with 99.999% purity was used as the initial powder sample. The fraction having particle size below 30 μm was isolated. The final fine particles were prepared by grinding in a bowl mill filled with alcohol. The fine particles thus prepared were annealed in a Pyrex tube filled with Ar gas at about 520 K for 25 minutes. In order to estimate an average crystallite size, the full width at half-maximum (FWHM) of the diffraction lines was measured. The average crystallite size was roughly estimated as 1.4 μm .

The x-ray powder diffraction data were collected by a MAC Science M18XHF-SRA-type diffractometer equipped with a curved pyrolytic graphite monochromator in a diffracted beam. The x-ray source used was Cu $K\alpha$ radiation with a tube voltage of 40 kV and a tube current of 200 mA. The x-ray powder diffraction patterns were recorded in steps of 0.02° in 2θ , and the counting time at each point was 100 s, in order to obtain a good counting statistics. The scan range in 2θ was from 20° to 120° and 11 independent reflections and 2 overlapping reflections of 511, 333 and 600, 442 were observed in these experimental conditions.

3. Analysis

The integrated intensities of the respective reflections were evaluated via a whole-powder-pattern fitting with the computer program WPPF by Toraya [6], in which a split Pearson-VII function was adopted as a profile function. In the analysis, the integrated intensity, peak position, full width at half-maximum, asymmetric factor and decay rate of each reflection were treated as independent parameters. Next, the scale factor had to be determined in order to convert the integrated intensities thus obtained into the structure factors on an absolute scale. This was done by a least-squares analysis using the computer program POWLS [7]. In the analysis, only the integrated intensities of the 11 independent reflections were used. The crystal structure of γ -CuBr is of sphalerite type (space group $F\bar{4}3m$) with Cu and Br on sites 4c ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) and 4a (0, 0, 0), respectively; therefore the parameters that have to be refined in the analysis are the scale factor and the isotropic temperature factors of the respective atoms. The observed independent structure factors are easily calculated from the observed integrated intensities with the aid of the scale factor. The structure factors thus determined include the effect on the anomalous dispersion; therefore the effect was eliminated from the structure factors by using the values tabulated in [8]. The corrected structure factors were used as the input data for the MEM analysis. However, γ -CuBr does not have inversion symmetry. Therefore, the phases of the corrected structure factors must be solved through the MEM analysis. We adopted the phases determined from the crystal structure using POWLS as the initial input data of the MEM. The procedure of the MEM calculation is the same as in previous reports [9–13]. In the actual calculation, the computer program MEED given by Kumazawa *et al* [14] was used, and the number of pixels was $64 \times 64 \times 64$.

4. Results and discussion

The final result of the least-squares analysis using POWLS is given in table 1 together with the R -factor and the weighted factor R_w and the estimated standard deviation in parentheses. The root mean square displacements of Cu and Br atoms calculated from the isotropic temperature factors are given in table 2, together with the results of previous measurements via neutron diffraction. Though the values were determined using different methods, based on different scattering amplitudes, the agreement between them was good. The Cu and Br ions in CuBr exhibit large thermal motions and the values are comparable to those of normal ionic solids near the melting point.

Table 1. A summary of the results of the least-squares analysis performed using POWLS.

Number of data used in the POWLS analysis	11
Isotropic temperature factor of Cu (\AA^2)	3.88(16)
Isotropic temperature factor of Br (\AA^2)	1.98(8)
Scale factor	0.74(10)
R -factor	0.011
Weighted factor, R_w	0.024

Table 2. Root mean square displacements of Cu and Br atoms obtained by different methods: neutron single-crystal diffraction (NSD); neutron powder diffraction (NPD); and x-ray powder diffraction (XPD). The data were obtained at 300 K, 295 K and 293 K by NSD, NPD and XPD, respectively.

$\sqrt{\langle U_{\text{Cu}}^2 \rangle}$	$\sqrt{\langle U_{\text{Br}}^2 \rangle}$	Method	Reference
0.210	0.167	NSD	[2]
0.212	0.156	NPD	[4]
0.220	0.156	XPD	Present

The absolute values of observed and calculated structure factors determined by the final MEM density distribution are given in the second and third columns in table 3, respectively, where the values in parentheses indicate the estimated standard deviation. In the last two columns, the values of real and imaginary parts of the calculated structure factors are also given. The calculated structure factors of the overlapping reflections were estimated from the final MEM densities, though the observed values of these reflections were not used in the MEM analysis. In the present calculation, the values of the R - and R_w -factors attained in the final MEM calculation were 0.008 and 0.01, respectively. The agreement of observed and calculated structure factors is very good, though the information to be obtained from experiments on powders, as compared with single-crystal experiments, is limited because the number of observable reflections is lower and some peaks overlap. The electron density map for the $(\bar{1}10)$ plane is shown in figure 1. The covalent chemical bonding between Cu and Br atoms is obvious. This corresponds to the strong admixture of the Cu 3d and Br 4p states as indicated by Christensen *et al* [5], though the electron density at the midpoint between Cu and Br atoms is somewhat different. Of course, their calculation was based on the ground state, and therefore anharmonic atomic vibrations were not considered. On the other hand, the electron density distribution of the present MEM map cannot be explained by considering only the chemical bonding. The valence electron density of Cu is elongated

Table 3. The absolute values of the observed structure factors F_{obs} , and the calculated structure factors F_{calc} from the MEM density distribution. The real and imaginary parts of the calculated structure factors are shown in the last two columns.

hkl	$ F_{\text{obs}} $	$ F_{\text{calc}} $	F_{calc}	
			Real	Imaginary
111	146.8(11)	144.4	112.80	-90.08
200	22.7(3)	22.7	22.69	0.00
220	159.0(12)	158.9	158.91	0.00
311	100.8(8)	100.5	82.41	57.54
222	24.2(6)	24.2	24.22	1.06
400	108.0(10)	109.1	109.12	0.00
331	73.5(6)	74.1	62.84	-39.21
420	24.8(5)	24.7	24.75	0.00
422	86.6(8)	86.2	86.21	-1.01
440	67.8(9)	67.2	67.19	0.00
531	45.0(6)	45.1	40.86	19.02
511		54.8	48.52	-25.56
333		59.1	51.89	28.25
600		21.2	21.23	0.00
442		20.1	20.05	0.83

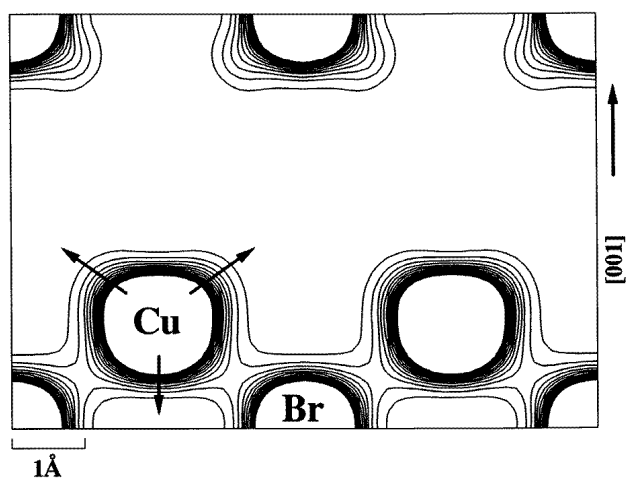


Figure 1. The MEM map of electron density for a plane in CuBr. The density region between 0.3 and 3.1 electrons \AA^{-3} is shown in intervals of 0.2 electrons \AA^{-3} . Three arrows indicate the extension directions of the electron density distribution.

in three directions indicated by arrows. This may be due to the low anisotropic potential of the Cu atom [2]. According to the results of neutron powder diffraction measurements by Altorfer *et al* [4], the nuclear density of Cu in γ -CuBr strongly extends along the same directions, except for the chemical bonding, as shown in the present MEM map. Therefore, the electron density distribution of Cu in γ -CuBr is well explained in terms of the anharmonic thermal motion and the chemical bonding due to hybridized Cu 3d and Br 4p states.

5. Concluding remarks

The electron density distribution map of γ -CuBr was found from a combination of x-ray powder diffraction data and the MEM. The MEM map obtained is well explained by the overlapping of the chemical bonding and anharmonic thermal vibrations. The root mean square displacements of Cu and Br determined by x-ray diffraction agreed well with those determined previously by neutron diffraction. We revealed that information on anharmonicity can be obtained from x-ray powder diffraction data with the aid of the MEM.

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