The assistance of Dr James Sawyer who prepared the Guinier photograph, and of Dr B. Morosin who made the crystallographic program available, is gratefully acknowledged. All calculations were performed at the Arizona State University Computer Center on a CDC 3400 computer.

References

Crystal Structure Calculations System, X-ray 63 (1964). Technical Report TR-64-6 NsG-398, Computer Science Center, University of Maryland, College Park, Maryland, U.S.A.

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Jonassen, H., Crumpler, T. & O'Brien. T. D. (1945). *J. Amer. Chem. Soc.* **67**, 1709.

Morosin, B. & Lingafelter, E. C. (1961). *J. Phys. Chem.* **65**, 50.

Willett, R. D. (1964). *J. Chem. Phys.* **41**, 2243.

Willett, R. D., Liles, O. L. Jr & Michelson, C. (1967). *Inorg. Chem.* **6**, 1885.

Zaslow, B. & Ferguson, G. L. (1967). *Chem. Commun.* p. 822.

Acta Cryst. (1971). **B27**, 852

Crystallographic polarity determination of γ-CuI.

By A. S. Bhalla and E. W. White, *Materials Research Laboratory, The Pennsylvania State University, University Park, Pa.* 16802, *U.S.A.*

(*Received* 14 *March* 1970 *and in revised form* 7 *July* 1970)

The polarity of single crystals of CuI having the sphalerite structure was determined from intensities measured on a double-crystal X-ray spectrometer, making use of anomalous scattering. If the direction from Cu to I is defined as [111], the results confirm that the (111) plane contains Cu^+ ions while the $(\bar{1}\bar{1}\bar{1})$ plane contains I^- ions, and that the natural faces of the tetrahedral crystals are of the type $(\bar{1}\bar{1}\bar{1})$.

Halides of Cu^+ have the sphalerite structure with space group $F\bar{4}3m$. The positive sense of the [111] direction is defined from Cu^+ to the halide ion, when Cu^+ is considered at position (0,0,0) and the halide at position $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. The opposite faces (111) and $(\bar{1}\bar{1}\bar{1})$ of this type of structure behave differently with regard to oxidation (Lavine, Rosenberg & Gatos, 1958) and etching (Maringer, 1958; Schell, 1957) and show differences in the integrated X-ray intensities (Coster, Knol & Prins, 1930) of reflection (Coster, Knol & Prins, 1930; Geib & Lark-Horowitz, 1932). The crystallographic polarity of CuCl and CuBr was established by Monier & Kern (1955). In this note results on γ-CuI are reported and correlated with the above definition of the [111] direction.

Crystals of γ-CuI (1 mm diameter) were used for experimental measurements on a double crystal X-ray spectrometer (Bhalla & White, 1970) having a finely collimated beam diameter smaller than the size of the crystal. Table 1 shows the calculated and measured intensity ratios from the two opposite faces, perpendicular to [111], for different orders of diffraction.

The observed ratios are very close to the calculated values. The X-ray conditions (counting time, current and voltage) were identical only while comparing a particular pair (*hkl*) and $(\bar{h}\bar{k}\bar{l})$.

Calculations were made considering Cu^+ at (0,0,0) and I^- at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and using the formula (Warekois & Metzger, 1959):

$$|F_n|^2=16[f_{\rm Cu}+f_{\rm I}e^{ix}]\,[f^*_{\rm Cu}+f^*_{\rm I}e^{-ix}]$$

where $f_{\rm Cu}=f^0_{\rm Cu}+\Delta f'_{\rm Cu}+i\Delta f''_{\rm Cu}$ *etc.* Asterisk symbols are the conjugate values of the complex quantities, and

$$x=2\pi\frac{3n}{4}\,,\ n=\pm 1,2,3\,.$$

Values of f°, $\Delta f'$ and $\Delta f''$ were taken from *International Tables for X-ray Crystallography* (1967) and calculated for the appropriate order of diffraction.

The peaks, scanned from (111) and $(\bar{1}\bar{1}\bar{1})$ faces, were found to have different full widths at half maximum. (Three sets of observations for first, second and third orders, in seconds of arc, are: 50 and 35, 31 and 33, and 38 and 54 respectively.) These differences could be explained qualitatively from the prediction of the Darwin theory that, for a small angle of reflection from a perfect, non-absorbing crystal, the peak half width at half maximum ω, in radians, is related to the structure factor as given by (Compton & Allison, 1935).

$$\omega=2{\cdot}8\,\delta FZ^{-1}\csc 2\theta_0\,.$$

Table 1. *Calculated and measured ratios of integrated intensities from opposite faces of* γ-CuI *single crystal for* Cr *Kα radiation*

	Total counts (above background)		$\frac{FF^*(hkl)}{FF^*(\bar{h}\bar{k}\bar{l})}$	
hkl	*hkl*	$\bar{h}\bar{k}\bar{l}$	measured	calculated
(111)	4332	2869	1·510	1·608
(222)	1995	2029	0·983	1·000
(333)	809	1723	0·470	0·507

(In the parallel setting of the double crystal X-ray spectrometer, Z = total number of electrons in the unit cell, θ_0 is the Bragg angle and δ is the unit decrement of refractive index of the crystal.)

These X-ray diffraction intensity and peak width measurements show that the (111) plane of γ-CuI contains Cu^+ ions while the $(\bar{1}\bar{1}\bar{1})$ plane contains I^-. Moreover, the studies showed that the natural faces of the tetrahedral crystals were of the $(\bar{1}\bar{1}\bar{1})$ index. This study demonstrates the feasibility of working with single crystals as small as 1 mm in diameter for direct crystallographic polarity determinations using a double crystal X-ray spectrometer.

The authors wish to thank Dr A. F. Armington of Air Force Cambridge Research Laboratory (OAR) for providing the crystals. This research was supported by Air Force Materials Laboratory, Air Force Systems Command, United States Air Force, under Contract No. F33615-67-C-1047.

References

Bhalla, A. S. & White, E. W. (1970). *Advanc. X-ray Anal.* **13**, 272. New York: Plenum Press.

Compton, A. H. & Allison, S. K. (1935). *X-ray Theory and Experiment*, p. 728, New York: Van Nostrand.

Coster, D., Knol, K. S. & Prins, J. A. (1930). *Z. Physik*, **63**, 345.

Geib, I. G. & Lark-Horowitz, K. (1932). *Phys. Rev.* **42**, 908.

International Tables for X-ray Crystallography (1967). Vol. III, pp 213–216. Birmingham: Kynoch Press.

Lavine, M. C., Rosenberg, M. C. & Gatos, H. C. (1958). *J. Appl. Phys.* **29**, 1131.

Maringer, R. E. (1958). *J. Appl. Phys.* **29**, 1261.

Monier, J. C. & Kern, R. (1955). *C.R. Acad. Sci. Paris*, **241**, 69.

Schell, H. A. (1957). *Z. Metallk.* **48**, 158.

Warekois, E. P. & Metzger, P. H. (1959). *J. Appl. Phys.* **30**, 960.

Acta Cryst. (1971). B**27**, 853

Ce_2O_2Sb and Ce_2O_2Bi crystal structure.*

By R. Benz, *Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico* 87544, *U.S.A.*

(*Received* 31 *August* 1970)

Ce_2O_2Sb and Ce_2O_2Bi crystals were prepared with body-centered tetragonal (U_2N_2Sb type structure, space group I4/*mmm*) unit-cell parameters

	a_0	c_0	u
Ce_2O_2Sb	4·012 ± 0·001 Å	13·697 ± 0·008 Å	0·344 ± 0·003
Ce_2O_2Bi	4·034 ± 0·001	13·736 ± 0·002	0·344 ± 0·003

Compounds with the chemical formula Ce_2O_2X, X = Sb and Bi, were prepared by reaction of weighed quantities of fused Ce_2O_3 + Ce and of elemental X in sealed silica capsules for one month at 800°. X-ray diffraction powder patterns of the two products could be indexed on the basis of tetragonal symmetry. Unit-cell dimensions and densities calculated for two molecules per unit cell are listed in Table 1.

The powder patterns are similar to that of the U_2N_2Sb type previously reported for U and Th compounds (Benz & Zachariasen, 1970) and to Ce_2O_2Te (Pardo & Flahaut, 1962). Accordingly, the structure is

Space group $I4/mmm$ (D_{4h}^{17})
$(000)\ (\frac{1}{2}\frac{1}{2}\frac{1}{2}) + 2X$ on (000)
$4Ce$ in $\pm(00u)$
$4O$ in $\pm(\frac{1}{2}0\frac{1}{4})$

where from observed intensities the parameter value was

Table 1. *Lattice-parameter data and densities of* Ce_2O_2X *compounds*

	a_0	b_0	u	v	Reference	Density (g.cm^{-3})
Ce_2O_2Sb	4·012 ± 0·001 Å	13·697 ± 0·008 Å	0·344 ± 0·003	—	This work	6·540 ± 0·007
Ce_2O_2Bi	4·034 ± 0·001	13·736 ± 0·002	0·344 ± 0·003	—	This work	7·747 ± 0·02
Ce_2O_2Te	4·0705 ± 0·0006	12·904 ± 0·002	0·344 ± 0·003	—	This work	6·835 ± 0·004
	4·09	12·92			Pardo & Flahaut (1962)	6·76
Ce_2O_2S	4·001 ± 0·002	6·844 ± 0·006	0·278 ± 0·003	0·63	This work	6·028 ± 0·01
	4·01 ± 0·01	6·83 ± 0·03	0·29 ± 0·02	0·64	Zachariasen (1949)	5·99
	4·00	6·87	—	—	Flahaut & Guittard (1955)	6·00
	4·004	6·872	—	—	Picon & Patrie (1956)	6·00
	4·008	6·886	0·208	0·863	Flahaut, Guittard & Patrie (1958)	5·98
Ce_2O_2Se	4·0152 ± 0·0003	7·0492 ± 0·0009	0·293 ± 0·003	0·63	This work	6·603 ± 0·002
	4·04 ± 0·01	7·06 ± 0·01	—		Benacerraf, Guittard, Domange & Flahaut (1959)	6·51

---

* Work done under the auspices of the U.S. Atomic Energy Commission.