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**Micro-photometry by scattered light.** By W. EHRENBURG and M. O. NORRIS\*, *Birkbeck College, Malet Street, London, W.C.1.*

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The quantitative evaluation of photographically recorded X-ray interference patterns based on micro-photometry of the processed film suffers from the non-linear relation between the light transmitted of which the density is an inverse function, and the X-ray dose received by the film. As a result, the quantitative evaluation of diffraction spots is a rather formidable problem. About 30 years ago Brentano, Baxter and Cotton pointed out that, within a reasonable range, a linear relation should exist between the light scattered by the grains and the X-ray dose; their experiments showed, however, that the fraction of scattered light was truly linear only for low densities below perhaps 0.2 and then tailed off. This linear range was too small to make the method practicable. The authors quite rightly attributed this failure to the fact that light, in order to be scattered, must also penetrate the film and therefore suffer attenuation by absorption. No further thought seems so far to have been given to getting over this difficulty (Buerger, 1960).

It occurred to us that changing the silver grains into transparent crystals of high refractive index would enhance the scattering and reduce the absorption. Reactions of this kind are parts of well known intensification or reduction techniques; of the ones we tried bleaching the film in a solution of 6g mercuric chloride and 6g potassium bromide

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in 250 ml water was best. When this bleaching procedure was combined with the measurement of the intensity of light scattered backwards, instead of the light scattered forwards, the meter reading was found to be linear with density (as determined before bleaching) up to densities of about 1.1.

There is far less light scattered backwards (at about 120°) than forwards (at about 20°) but no difficulty arises from this if a photomultiplier is used. It was found necessary, however, to place the film in immersion oil or Canada balsam between a clear and a blackened glass plate in order to prevent primary and forward scattered light from being reflected backwards at film-glass-air interfaces.

The light received by the photomultiplier is then a measure of the X-ray dose that has fallen onto the illuminated area; obviously, allowance must be made for scattering by the blank film. The modification of Brentano's method here proposed offers therefore the prospect of a simple and reliable method of measuring integrated intensities such as are recorded by a rotating crystal, Weissenberg and similar photographs.

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**Lattice constants of the ternary ordered alloys AgAuCd<sub>2</sub>, AgAuZn<sub>2</sub>, and CuAuZn<sub>2</sub>\***. By L. MULDAWER, *Temple University, Philadelphia, Pa. 19122, U.S.A.*

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Ternary ordered structures have been observed around the stoichiometric compositions for the alloys AgAuCd<sub>2</sub>, AgAuZn<sub>2</sub>, and CuAuZn<sub>2</sub>. The last alloy was first independently reported by Schubert, Burkhardt, Esslinger, Günzel, Meissner, Schütt, Wegst & Wilkens (1956), and more recently by Duggin & Rachinger (1964), who studied a nonstoichiometric alloy, 31.2% Cu, 23.5% Au, 45.3% Zn. Rothwarf & Muldower (1962) observed ternary ordering of gold-silver over a wide range of composition near AgAuCd<sub>2</sub>. In all three alloys, the noble metal order gradually disappears as the temperature is raised (Muldawer, 1966).

Visual intensity observations of the powder patterns and lattice constant measurements indicate that the three ternary phases have the Heusler alloy structure (*L21*), space group *Fm3m*, with the noble metals ordered in positions 4(*a*) and 4(*b*) and Zn or Cd occupying positions 8(*c*), 16 atoms per unit cell. These ternary alloys differ from most of the other

Heusler alloys in that the compound ABC<sub>2</sub> is made up of binary compounds AC and BC. The only other compound satisfying this requirement known to this author is Ni<sub>2</sub>TiAl (Taylor, 1961).

Lattice constants of these alloys were determined from precision measurement of powder pattern lines. The values reported in Table 1 are the average of several determinations, each of which was obtained using a Nelson-Riley extrapolation. It is believed that these results are good to one part in 10<sup>4</sup>. Included in the table is the value reported by Duggin & Rachinger for their alloy.

Table 1. *Lattice constants of alloys*

Compositions are in at. %.

The last alloy is that of Duggin & Rachinger.

Alloy	Composition			Lattice constant
AgAuCd <sub>2</sub>	24.82,	25.11,	50.07	6.6462 Å
AgAuZn <sub>2</sub>	26.02,	25.21,	48.77	6.2943
CuAuZn <sub>2</sub>	24.72,	25.22,	50.06	6.1273
CuAuZn <sub>2</sub> (DR)	31.2,	23.5,	45.3	6.098

\* A preliminary report of these alloy structures was presented at a meeting of the American Crystallographic Association, June 1962.

Calculations were made of the lattice constants of these alloys expected on the basis of weighted averages of the binary lattice constants. For example, in the case of  $\text{AgAuZn}_2$ , this meant determining the lattice constants of  $\beta\text{-AgZn}$  (48.8% Zn) and  $\beta\text{-AuZn}$  (48.8% Zn). Most of the constants were obtained from plots of the data found in Pearson (1958);  $\beta\text{-AuZn}$  values were taken from a recent unpublished study in this laboratory. Table 2 gives the results and shows the differences between observed and calculated lattice constants. It can be seen that  $\text{AgAuCd}_2$  and  $\text{AgAuZn}_2$  contract about 0.2% while  $\text{CuAuZn}_2$  expands 0.3%. Contraction is expected when ordering occurs; the expansion in the case of  $\text{CuAuZn}_2$  seems unusual. This result is no artifact since it is observed in this work and that of Duggin & Rachinger.

Table 2. Observed and calculated average lattice constants

Alloy	$a_{\text{obs}}$	$a_{\text{calc}}$	$\Delta a$
$\text{AgAuCd}_2$	6.6462	6.6600	-0.014 Å
$\text{AgAuZn}_2$	6.2943	6.3097	-0.015
$\text{CuAuZn}_2$	6.1273	6.1092	+0.018
$\text{CuAuZn}_2(\text{DR})$	6.098	6.080	+0.018

Cold working of  $\text{AgAuZn}_2$  completely destroys the ternary long range order; this order is restored by long anneals at room temperature or by a brief anneal at a relatively low temperature. Cold-working of  $\text{AgAuCd}_2$  and  $\text{CuAuZn}_2$  reduces the ternary order and produces either a face-centered cubic or close-packed hexagonal martensitic phase as well. The martensitic phase is removed and ternary order recovered by mild anneals as above. Quenching is capable of preserving some disorder in only  $\text{AgAuZn}_2$ .

The most striking feature of these alloys is the ordering of Ag-Au in the alloys  $\text{AgAuCd}_2$  and  $\text{AuAgZn}_2$  since no long range ordering occurs in the binary AgAu. Rotwarf & Muldower have suggested that a possible cause for this ternary Ag-Au ordering may be found in an enhancement of the Ag-Au ion core potential difference by the zinc or cadmium 'atmosphere'. The electronegativities of Zn and Cd are such that some ionicity is expected in alloys made up of IB and IIB elements and the amount of the ionicity

will very likely be different in  $\beta\text{-AgCd}$  and  $\beta\text{-AuCd}$ . This could then be the mechanism for producing ternary Ag-Au ordering. A genuine understanding of the silver-gold ordering in these ternaries will probably be found in the more general approach of Harrison & Paskin (1962). In their polar model of order-disorder, they show that there is an oscillating potential with the energy of ordering dependent upon lattice constant and Fermi energy. Thus, a different Ag-Au ordering energy would hold in the case of AgAu relative to  $\text{AgAuCd}_2$  or  $\text{AgAuZn}_2$ .

The ternary ordering in  $\text{CuAuZn}_2$  is not surprising since the alloy CuAu exhibits long range order below 410°C. A possible explanation for the expansion of  $\text{CuAuZn}_2$  over the expected average value may lie in the fact that the 'size' of the gold atoms prevents too great a shrinkage of the Au-Zn distance. The gold and copper 'sizes' are quite different (7%) while the gold and silver 'sizes' are almost the same.

The experimental parts of this study have been carried out with the aid of a number of student assistants. Appreciation is expressed for the continued support of the U.S. Atomic Energy Commission.

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**Crystal data for triclinic dicyclopentadienyl-lead.** By G. BOMBIERI and C. PANATTONI, *Centri Chimica Radiazioni Radiolementi e Strutturistica Roentgenografica del C.N.R., Padova, Italy*

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We have prepared dicyclopentadienyl-lead,  $(\text{C}_5\text{H}_5)_2\text{Pb}$ , following the Fisher (1956) method, and have obtained two crystalline modifications by sublimation in vacuum.

Form 1 was yellow and form 2 was brown-yellow. Crystals of both forms were unstable in the air. We have examined by X-ray crystallography single crystals of both forms kept under nitrogen in Lindemann glass.

Form 1 proved to be orthorhombic; its structure determination has been completed (Panattoni, Bombieri & Croatto, 1966).

The habit of form 2 is prismatic. The cell-dimensions are:

$$\begin{aligned} a &= 8.42 \pm 0.02 \text{ \AA} & \alpha &= 94^\circ 27' \pm 30' \\ b &= 10.61 \pm 0.03 & \beta &= 96^\circ 58' \pm 30' \\ c &= 15.92 \pm 0.02 & \gamma &= 90^\circ 7' \pm 30' \end{aligned}$$

All the expected reflexions are observed; the space group is triclinic  $P1$  or  $P\bar{1}$ . No further work on this form is contemplated.

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