length increases initially at the rate of 0·2 Å/°C. At higher temperatures the rate of increase is greater and by 200 °C the wavelength for isotropy is 5030 Å.

Conclusion

Direct observation of optical activity substantiates the theory of optical activity based upon the gyration tensor for the crystal class $\bar{4}2m$. This positive observation provides the first recorded instance of optical activity in a non-enantiomorphous crystal.

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The Structures and Phase Transformations in β-AuCd Alloys

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An X-ray powder diffraction and single-crystal study of the structures and phase transformations existing in the 50 at.% region of the gold–cadmium system has been carried out. The transformation β_1 (cubic)$\rightarrow\beta'$ (orthorhombic) occurring in the range 47–48·5 at.% Cd is confirmed. At higher cadmium content, 49–52 at.%, the cubic β_1 phase transforms to a structure possessing hexagonal symmetry rather than the previously suggested tetragonal structure. The X-ray diffraction patterns of this hexagonal structure can be interpreted in terms of a unit cell of 27 atoms, which is structurally similar to the ξ phase of the AgZn system.

Introduction

Above 80 °C gold–cadmium alloys of around 50 at.% composition have an ordered body-centred cubic structure (a=3·3126 Å), the β_1 phase. Below 80 °C, the β_1 phase is subject to two possible structural modifications. Alloys in the range 47–48·5 at.% Cd transform to give a product phase β' which is said to have an orthorhombic structure (Ölander, 1952*a*,*b*; Chang, 1951). At higher cadmium content, 49–52 at.%, alloys transform to a phase β'' which is reported to have a tetragonal structure by Köster & Schneider (1940) and Chen (1954).

The transformations take place on cooling at 60 °C and 30 °C and on heating at approximately 80 °C and 40 °C respectively.

The structure of the β' phase is fairly well established. Ölander was able to show that most of the X-ray powder diffraction lines could be explained on the basis of an orthorhombic structure, having cell parameters a=3·144, b=4·851, c=4·745 Å.

The structure of the β'' phase is less certain. Köster & Schneider gave tetragonal cell parameters for the β'' phase as: a=5·074, c=4·487 Å. This was supported by Chen, who was uncertain of the actual lattice parameters but suggests the unit cell is large, with the possible parameters shown in Table 1.

There has been considerable interest in the mechanisms of the transformations, which possess some unusual features. The phase changes take place athermally and the product phases indicated are those resulting from slow or moderately slow cooling rates from the parent phase. The transformation mode, and in certain cases the transformation product, may be altered by suitable heat treatment of the parent phase. A number of investigations have been carried out using resistivity and elastic moduli data to study these effects (Wechsler, 1957; Subramanya, Baker, Lieberman & Read, 1961; Zirinsky, 1956; Class & Lieberman, 1961; Birnbaum, 1959). The results of these investigations are summarized below:

(1) Following severe quenching, alloys in the range 47–48·5 at.% Cd transform to produce resistivity and elastic data similar to those recorded during the transformation $\beta_1 \rightarrow \beta''$. From this observation, it was concluded that the $\beta_1 \rightarrow \beta'$ transformation is inhibited by

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severe quenching in favour of a new transformation $\beta_1 \rightarrow \beta'''$.

(2) Because of the similarity between the transformation characteristics of this new phase change $\beta_1 \rightarrow \beta'''$ and the change $\beta_1 \rightarrow \beta''$ occurring in the higher cadmium alloys, it was thought that the two products β''' and β'' might be structurally similar. However, according to Zirinsky, the presence of this quench-induced product β''' could not be detected in X-ray powder diffraction patterns.

(3) Alloys in both composition ranges 47–48·5 at.% Cd and 49–52 at.% Cd can be made to transform isothermally. This can be achieved either following a severe quench from the β_1 phase, or following long anneals in the β_1 phase just above the normal transformation temperatures. In either case isothermal

Table 1. *Results of the computer indexing of the β'' pattern, using as assumed parameters the parameters of Köster & Schneider and of Chen, and also using the hexagonal cell constants derived in this investigation*

(1) Tetragonal unit cell (Köster & Schneider): $a=5{\cdot}074$, $c=4{\cdot}487$ Å.
(2) Tetragonal unit cell (Chen): $a=3{\cdot}3356$, $c=3{\cdot}2887$ Å.
(3) Tetragonal unit cell (Chen): $a=10{\cdot}0068$, $c=9{\cdot}8661$ Å.
(4) Hexagonal unit cell refined parameters: $a=8{\cdot}1019$, $c=2{\cdot}9005$ Å.
(5) Hexagonal unit cell refined parameters: $a=8{\cdot}1031$, $c=8{\cdot}7033$ Å.
Composition of specimen used in this investigation: Au–50 at.% Cd.

	Indices *hkl*				
sin θ	Köster & Schneider	Chen		This investigation	
	(1)	(2)	(3)	(4)	(5)
0·2342		001	003		201
0·2895			312	101	103
0·2930		101	213	210	210
0·3286			303	111	113
0·3316			114	300	300
0·3468	201		204	201	203
0·3954			314	310	310
0·4049	112		115		311
0·4656			424	221	223
0·5325				002	006
0·5438			(710) (550)	102	106
0·5486	222		(505) (435)	500	500
0·5653		211	721	112	116
0·5701	302	112	525	411	413
0·5718			336	330	330
0·5819			722	420	420
0·6065	400		732	212	216
0·6108			516	510	510
0·6190				501	503
0·6260	410		526	302	306
0·6543		220	822	222	226
0·6596			803	600	600
0·6635			734	312	316
0·6673	331		(507) (437)	430	430
0·6728			517		431
0·7160			655	322	326
0·7210				610	610
0·7324		301	(815) (745)	412	416
0·7360			547	521	523
0·7800			618	332	336
0·7893			854		(702) (532)
0·8061			846	441	443
0·8136				(701) (531)	(703) (533)
0·8196			944	113	119
0·8355	521	302	961	621	623
0·8463	512		962	602	606
0·8536			629	432	436
0·8578	005		549	540	540
0·8625			865	303	309
0·8690				711	713
0·8713	105	213	639	630	630
0·8729			881		517
0·8786	324		847	800	800
0·8946			649	612	616
0·9175	(503) (433)			801	803

transformation always proceeds with the characteristics of the $\beta_1 \rightarrow \beta''$ transformation, irrespective of the alloy composition.

The present work investigates the transformation in these alloys and reexamines the crystal structures of the product phase, particularly the β'' phase and the quench-induced product β'''.

Experimental work

The purity of the metals used in making the alloys exceeded 99·99%. The metals were melted in an argon atmosphere at 1100°C. The samples were held in the liquid state for one hour, and then at a temperature 50°C below the melting point for three days. Finally, the temperature was lowered to 250°C from which point the alloys were quenched into iced water.

X-ray powder diffraction patterns were taken with a 19 cm camera and filtered Cu $K\alpha$ radiation ($\lambda K\alpha_1 = 1{\cdot}54050$ Å), and they were indexed using a computational procedure (Hoff, Wallace & Kitchingman, 1965).

In order to obtain single crystals of the low temperature phase it was necessary to grow large single crystals of the parent cubic phase. Transformation to the low temperature phase, on occasion, took place by formation of single crystals of the β'' product. This was favoured by use of well-annealed crystals of the β_1 phase, and by using as slow a cooling rate as possible through the transition range. Several good crystals were obtained, of average size about 1 cubic mm.

Results and discussion

A range of alloys with compositions from 46 by steps of 0·25 up to 53 at.% Cd were examined after quenching from 250°C. In the range 47–48·5 at.% Cd the β' pattern was found, whilst the range 49–52 at.% Cd gave the β'' pattern. Outside these ranges additional lines appeared, but were not identified. Intermediate compositions, 48·5–49 at.% Cd produced patterns having lines characteristic of both structures. An alloy of composition 47·5 at.% Cd quenched into iced water from temperatures of 150, 250, 300, 350, 450 and 500°C respectively showed a gradual change in pattern with increase in quenching temperature. Lines characteristic of the β''phase appeared at 300°C whilst at 500°C the normal transformation $\beta_1 \rightarrow \beta'$ was completely suppressed in favour of the transformation $\beta_1 \rightarrow \beta''$.

Attempts were made to index the X-ray patterns by the computer method with input data consisting of the previously published lattice constants and other relevant information. The results of some of these tests are summarized in Table 1.

In the case of the β' structure, the pattern could be indexed fully and the finally computed lattice parameter values are $a=4{\cdot}7690$, $b=3{\cdot}1437$, $c=4{\cdot}8717$ Å, in good agreement with those given by Chang. Indexing the pattern of the β'' structure was less successful, although the largest parameters suggested by Chen provided a near fit. A visual observation of the diffraction pattern of the β'' phase suggested that the structure is likely to be closely related to the structure of the parent β_1 phase since its powder pattern shows strong reflexions in positions of the lines of the β_1 phase, with small changes in position. The most intense diffraction lines of the β'' structure are produced by splitting reflexions of the β_1 structure; thus two strong reflexions occur, one on either side of the strong body-centred cubic 110 reflexion. It seems likely that the β'' structure is derived from its parent β_1 phase by small movements of the atoms from the positions occupied in the β_1 structure, and, in view of the large number of reflexions appearing in the powder pattern, it is likely that the structure possesses a large unit cell.

Several trial unit cells of the orthorhombic, tetragonal and hexagonal crystal systems were calculated, and used in turn as the initial lattice constants of the indexing program, in an attempt to find a satisfactory fit. The closest fit was obtained when the cubic structure was considered in terms of hexagonal or trigonal lattices. A body-centred cubic structure may be considered as a hexagonal structure having its c axis along one of the cube diagonals. The parameters of the cell are given by:

$$a=\sqrt{6}a_0 \quad \text{and} \quad c=\sqrt{\tfrac{3}{2}}a_0\,,$$

where a_0 is the lattice parameter of the body-centred cubic unit cell. This model was used by Edmunds & Qurashi (1951) in their derivation of the ζ phase structure in the AgZn system. Applying this to the gold–cadmium data, the lattice constants of the hexagonal cell produced are given by:

$$a=\sqrt{6}\times 3{\cdot}3126=8{\cdot}11\ \text{Å}\,,$$
$$c=\sqrt{\tfrac{3}{2}}\times 3{\cdot}3126=2{\cdot}86\ \text{Å}\,.$$

The results of the indexing program using these parameters are shown in Table 1. A good fit is obtained for the powder data, and although not complete this suggests that the actual unit cell is very closely related to this model. The values of lattice constants refined during the indexing routine are very close to the theoretical values, $\Delta a = -0{\cdot}0081$ Å and $\Delta c = +0{\cdot}041$ Å.

Laue patterns of several crystals were recorded; the patterns showed the presence of a threefold symmetry axis with three symmetry planes at 60° intervals. In all crystals examined, symmetry elements of this type could be located after suitable orientation. The only other symmetry axes which could be found were diad axes. These were located perpendicular to the triad axis, and were repeated about this axis at 60° intervals. These patterns also showed two perpendicular mirror planes. In spite of repeated examination of many crystals, no evidence of fourfold rotation axes could be found. This removes all possibility that the crystals might be tetragonal and also confirms that transformation from the cubic β_1 phase has taken place.

Oscillation photographs were subsequently taken of these crystals in order to determine the identity period of the lattice along the crystal axes found in the Laue examination. Because of the high absorption coefficients of the alloys, only a limited amount of data in the high angle region could be recorded. The formation of layer lines was clear in all photographs and provided information about the size of the unit cell. Three significant axes were examined in each case; the triad, or c axis, and the two principal axes perpendicular to the c axis, the a axis and that 30° to the a axis, for convenience referred to here as the b axis. Values of 8·100 Å and 7·020 Å were obtained for a and b which are mutually consistent, and in agreement with the a parameter calculated from the cubic lattice. The c parameter obtained from the single-crystal photograph was 8·698 Å, which is almost exactly three times the c parameter calculated previously.

These new a and c parameters were used as the trial constants in the indexing routine, the results of which are shown in Table 1. The lattice parameters of the β'' structure are finally given as $a = 8{\cdot}1031 \pm 0{\cdot}0005$ Å, and $c = 8{\cdot}7033 \pm 0{\cdot}0005$ Å at 20°C. The structure implied by these constants is likely to be closely related to the ζ phase of the AgZn and the AgGa systems save that the β'' AuCd lattice extends over three cell lengths of the conventional ζ phase structure and thus contains 27 unit cell atoms. A more detailed examination of the β'' structure is in progress.

The evidence shows that the β'' structure is thus not tetragonal and suggests either a trigonal or hexagonal unit cell. Although the Laue photographs clearly showed the symmetry elements of the structure, the reflexions were diffuse, indicating polygonization or the presence of multi-crystallites of almost identical orientation. This is significant, if the structure is similar to the ζ-AgZn structure. True single crystals of the ζ-AgZn structure have never been isolated, the transformation from the parent cubic β phase occurring by formation of many minute crystallites of ζ phase, having their c axes along the cube diagonals of the parent cubic grains.

The X-ray patterns obtained from quenched filings of any alloy containing 47·5 at.% Cd illustrate the change in type of transformation induced by quenching. Following sufficiently severe quenching the transformation product is the β'' structure. The change in mode of transformation is gradual, showing first signs of deviation in the 300°C quench, and complete change with the 500°C quench. It is concluded that the previously described $\beta_1 \rightarrow \beta'''$ transformation is really $\beta_1 \rightarrow \beta''$. There are indications however, in the powder photographs, that the change is not a simple switch from one transformation product to another ($\beta' \rightarrow \beta''$), but that it occurs by way of an intermediate structural type since the X-ray photographs of alloys quenched from 350°C and 400°C show strong reflexions which are not characteristic of either β' or β'' products.

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Specimen and Beam Tilt Errors in Bond's Method of Lattice Parameter Determination

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An analysis of the specimen and beam tilt errors in the Bond method of precision lattice parameter determination is presented. The assumption that the two are independent and thus additive is incorrect. Numerical values of the errors for some special cases are given.

A method of determining the lattice parameters of good-quality single crystals was described by Bond (1960). It is capable of (relative) accuracies of a few parts per million and it has been used when extreme precision is desirable (*e.g.* D'Heurle, Feder & Nowick, 1963). The arrangement is shown schematically in Fig. 1. Ideally the crystal is orientated with a suitable crystallographic plane parallel to the rotation axis of a divided circle and a well collimated beam of monochromatic X-rays normal to the rotation axis is diffracted into the detector A, when the crystal is in position a, and into the detector B when it is rotated to