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The Geometry of Twinning in $HoCu_2$

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Abstract

The twinning relationship in the intermetallic compound $HoCu_2$ was determined by single-crystal X-ray diffraction techniques. A 60° rotation about the *b* axis between the two components of the twins was found. The twin plane is (103). The measured single-crystal lattice parameters deviate from those obtained from powder data by 0.03 Å for *a* and 0.10 Å for *c*. These deviations may be due to strain in the structure caused by the twinning. The same twinning geometry is believed to hold true for the other rare-earth–metal (REM_2) intermetallic compounds with the KHg_2-type structure that exhibit massive twinning. This twinning may be the result of a high-temperature martensitic-type phase transformation.

Introduction

The microstructures of rare-earth–metal (REM_2; M = Cu, Zn) intermetallic compounds exhibit extensive twinning (Kejriwal, 1962; Chiotti, Mason & Gill, 1963; Chiotti & Mason, 1965, 1967; Mason & Chiotti, 1968; Michel & Ryba, 1969), the origin of which is thought to be a high-temperature martensitic-type transformation (Chiotti, Mason & Gill, 1963; Mason & Chiotti, 1968). In this paper, the results of a study are presented in which the twinning relationship in $HoCu_2$ was determined through the use of single-crystal X-ray diffraction techniques.

Most of the REM_2 compounds, including $HoCu_2$, exhibit the orthorhombic KHg_2- or $CeCu_2$-type structure (Duwell & Baenziger, 1955; Larson & Cromer, 1961). Storm & Benson (1963) determined the lattice parameters for $HoCu_2$ to be $a = 4.280$ (5), $b = 6.759$ (5) and $c = 7.290$ (5) Å, while Smetana, Síma & Lebech (1986) determined the atom positions (space group *Imma*) to be Ho: 4(*e*) [$z = 0.544$ (1)] and Cu: 8(*h*) [$y = 0.056$ (1), $z = 0.162$ (1)]. The structure, using these lattice and positional parameters, is shown in Fig. 1.

Experimental

A sample was prepared by sealing stoichiometric amounts of 99.5% Ho and 99.999% Cu in a tantalum crucible. The mixture was then melted, slowly cooled and finally annealed to homogenize the alloy. Crystal fragments chosen from this sample were coated with a polymer resin to suppress oxidation. A powder sample was prepared by crushing a portion of the alloy and passing the powder through a 325 mesh sieve; the powder pattern was run immediately after preparation of the sample. A step scan (0.02° step size, 4 s counting time) was performed over the range 15–120° 2θ on a Scintag powder diffractom-

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eter fitted with a solid-state counter, using Cu $K\alpha$ radiation ($\lambda_{K\alpha_1} = 1.54059$ Å).

Single-crystal X-ray diffraction studies showed that all crystal fragments were twinned. Two fragments were aligned so that an *a* axis and a *c* axis, respectively, were parallel to the rotation axis of a Weissenberg camera, and equi-inclination photographs (Fe $K\alpha$ radiation, $\lambda = 1.937355$ Å) were taken. The composite reciprocal lattices for each of these twinned crystals were plotted and separated into two component lattices. The relative orientation of the reciprocal lattices of the twins was thus established and used to determine the twin plane in direct space.

Lattice parameters were calculated from the powder diffraction data using the Cohen's method program *NBS-JCPDS-LSQ*85 (Hubbard, Lederman & Pyrros, 1985). Values of the *b* and *c* parameters for the twinned crystals were obtained from back-reflection Weissenberg data. The diameter of the back-reflection camera was 73.05 mm, and Fe $K\alpha_1$ ($\lambda = 1.936042$ Å), Fe $K\alpha_2$ ($\lambda = 1.939980$ Å) and Fe $K\beta$ ($\lambda = 1.75661$ Å) reflections were used. A total of 22 values for $0kl$ type reflections were analyzed using Cohen's method with the Nelson–Riley correction function.

Results and discussion

Oscillation photographs for the crystals oriented along the *a* and *c* axes contained extra layers of reflections with a resulting interlayer spacing, in reciprocal space, of half of the values calculated from the expected lattice parameters. These extra reflection layers are a result of the twinning in the crystals.

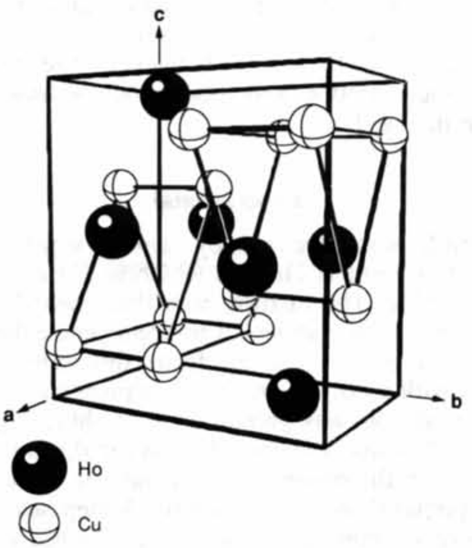

Fig. 1. Atom positions in a unit cell of $HoCu_2$.

The reflections in the equi-inclination photographs of both crystals were plotted. Two-dimensional cells chosen for these reciprocal-lattice levels were identical in shape and orientation but displaced by $\frac{1}{4}\mathbf{a}^*$, $\frac{1}{2}\mathbf{b}^*$ and $\frac{1}{4}\mathbf{c}^*$ with respect to one another. The centered even levels form the reciprocal lattice expected from an untwinned crystal, while the noncentered odd levels form an extra interpenetrating lattice. From the level sequence, looking down the a^* axis (Fig. 2), it can be seen that, due to the twinning, extra levels of reflections are produced that are perpendicular to the $\mathbf{a}^*$ and $\mathbf{c}^*$ directions but not to the $\mathbf{b}^*$ direction.

This observed reciprocal lattice is thus a composite of two identical lattices, one of which is rotated with respect to the other. A rotation about either the a^* or the c^* axis will not result in the formation of any

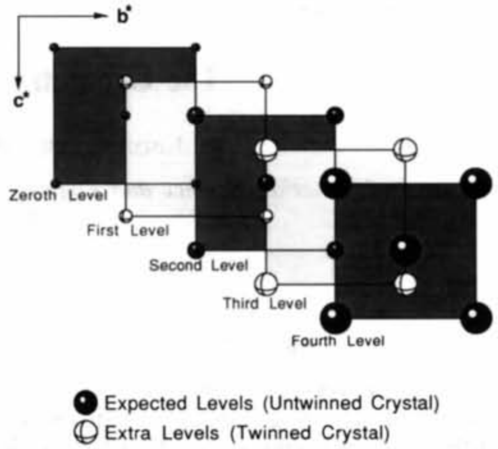

Fig. 2. Observed reciprocal-lattice levels of twinned $HoCu_2$ viewed down the a^* axis.

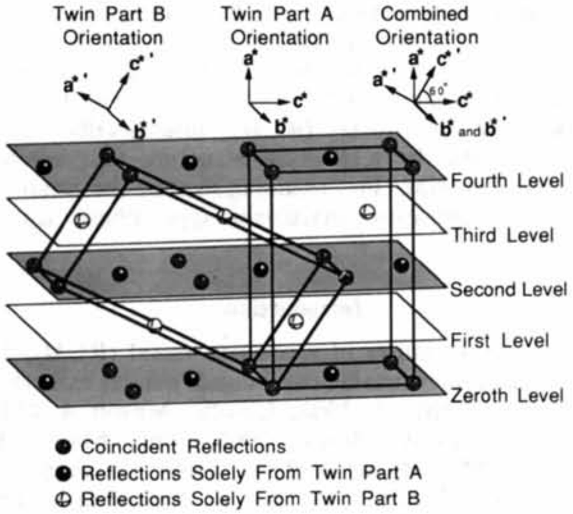

Fig. 3. Observed reciprocal lattice showing the orientation of the reciprocal-lattice cells for both twin parts. The extra levels (lightly shaded) result solely from twin part *B*.

extra reciprocal-lattice levels perpendicular to the **a*** or **c*** directions, respectively. Only a rotation about the b^* axis yields extra layers of reflections perpendicular to the **a*** and **c*** directions but not the **b*** direction, which agrees with our observations. Since the origin of both lattices must be coincident in reciprocal space and extra levels of reflections were observed perpendicular to only two directions, it was possible to determine the orientation relationship between the two parts of the twin. For both of these criteria to be met, the reciprocal cell for one part must be rotated almost exactly 60° with respect to the other about the common b^* axis. Fig. 3 shows the two interpenetrating reciprocal lattices for such an orientation relationship.

The same relationship between two parts of a twin, a 60° rotation around the b axis, is viable in both reciprocal and direct space for orthorhombic symmetry. Fig. 4 illustrates this in direct space; the twin plane is the (103) plane. If all the atoms at the twin boundary are coplanar, the Ho and Cu atoms on the boundary must shift approximately 0.3 and 0.04 Å, respectively, in the $\pm\mathbf{c}$ directions. If the twin plane is not truly planar or if the Ho atoms do not lie directly above one another along the **b** direction, such large shifts in the positions of the Ho atoms may not be required. It is probably not possible to predict the exact positions of the Ho and Cu atoms on and in the vicinity of the twin plane.

The lattice parameters determined from the powder pattern show quite good agreement with those of Storm & Benson (1963). On the other hand, while the b parameter from the single-crystal results closely matches the value given by Storm & Benson, the a and c parameters were found to be respectively 0.03 Å less and 0.10 Å greater than the values they reported (Table 1). If these results are correct, it would appear that the twinning introduces some type of strain into the crystal that influences the values of the a and c parameters but not the b parameter (probably because the b direction is coincident for both components of the twin). Unfortunately, it was not possible to calculate precise lattice parameters for each component of the twinned crystal since only two nonoverlapped reflections were visible on the back-reflection Weissenberg photograph.

Table 1. *Comparison of* $HoCu_2$ *lattice parameters*

	a (Å)	b (Å)	c (Å)
Storm & Benson (1963) (powder method)	4.280 (5)	6.759 (5)	7.290 (5)
This work (powder method)	4.284 (2)	6.777 (3)	7.292 (3)
This work (single crystal)	4.25 (1)	6.775 (2)	7.389 (3)

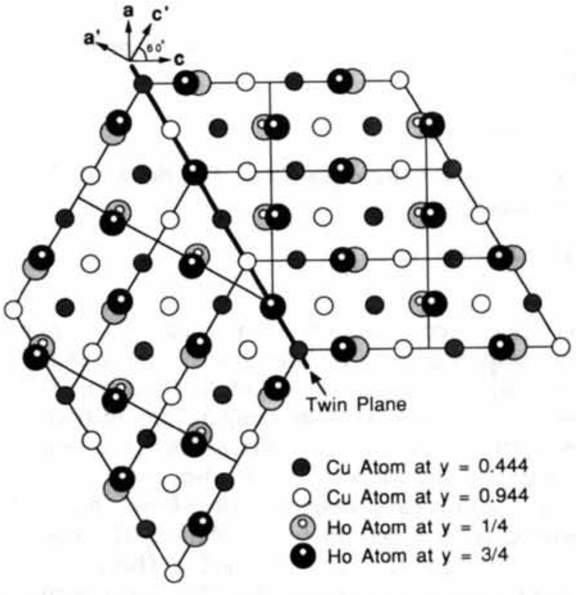

Fig. 4. Direct-space orientation of $HoCu_2$ twin parts viewed down the b axis. The Ho atoms are shown as having shifted to the twin boundary.

The differences in the a and c lattice parameters may be due to the fact that the single crystals used in this study were obtained by crushing the bulk sample, while the powder was prepared by extensive grinding. Michel & Ryba (1969) found that $HoZn_2$, with a twinned microstucture similar to that in Fig. 5, exhibits additional twinning when deformed. Grinding may create considerably more twinning than the crushing used to obtain single crystals. The powder would then contain a larger ratio of twin-boundary volume to perfect-crystal volume than the single crystals.

To understand completely the nature of the twinning, it is necessary to make further studies of

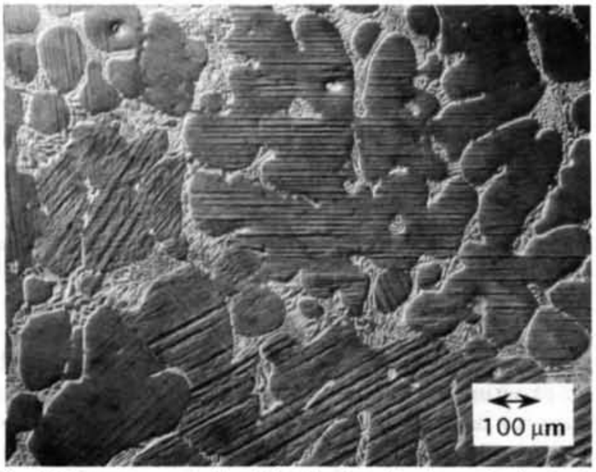

Fig. 5. Microstructure of an Ho–Cu alloy showing twinning in the main phase, $HoCu_2$. Polarized light; 3% nital etch.

the high-temperature structure of $HoCu_2$, suggested by Amin (1974) to be the $NdAu_2$-type structure (as yet undetermined), the transformation responsible for the twinning and the room-temperature lattice parameters of untwinned single crystals.

Since most REM_2 (M = Cu, Zn) compounds are isostructural with KHg_2, are chemically similar and exhibit massive twinning, it is probable that they exhibit the same twinning geometry as $HoCu_2$.

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Atomic Thermal Parameters and Thermodynamic Functions for Chrysoberyl ($BeAl_2O_4$) from Vibrational Spectra and Transfer of Empirical Force Fields

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Abstract

Using empirical atomic charges and valence force fields derived from a best fit to the Raman–IR spectra, and applying a rigid-ion Born–von Karman model, atomic thermal parameters have been calculated for chrysoberyl ($BeAl_2O_4$). The agreement with the experimental values (redetermined here for this purpose) is good; and excellent agreement with the experimental data is obtained for the estimates of some thermodynamic functions such as entropy and the molar heat. As for other oxides and silicates, the zero-point contribution is particularly important with respect to both the vibrational energy and to the mean-square amplitude of motion (about 83 and 70% of the value at room temperature, respectively). In order to test transferability of the force fields, the vibrational frequencies have also been calculated using empirical valence force-field parameters derived from a best fit to the Raman–IR spectra of corundum (Al_2O_3) and bromellite (BeO), without fitting the chrysoberyl spectra. The agreement with the experimental values is good, especially for the low frequencies. However, there is significant dis-

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