JOURNAL OF SOLID STATE CHEMISTRY 73, 591–592 (1988)

On the Structure of $ZnIn_2Se_4$

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Received June 8, 1987; in revised form October 23, 1987

The crystal structure of $ZnIn_2Se_4$, originally described in space group $I\bar{4}$, is properly described in $I\bar{4}2m$. In the revised description, four of the (disordered) metal atoms lie in equivalent sites of symmetry $\bar{4}$, two lie in sites of symmetry $\bar{4}2m$, and the Se atoms lie on mirror planes; the Laue symmetry is $4/mmm$ rather than $4/m$. © 1988 Academic Press, Inc.

The structure of $ZnIn_2Se_4$ has recently (*1*) been described in space group $I\bar{4}$ (tetragonal; $a = 5.705(2)$, $c = 11.448(3)$ Å, $Z = 2$, Laue symmetry $4/m$) and refined to $R = 0.079$ for 566 reflections. The structure consists of selenium atoms in positions approximating cubic closest packing with zinc and indium atoms randomly distributed in three-eighths of the tetrahedral holes.

There has been considerable discussion over the proper space group description of this class of compounds, beginning with the early work of Hahn *et al.* (*2*) whose powder-diffraction data could not differentiate between the two Laue groups $4/m$ and $4/mmm$. The present (*1*) single-crystal data presumably could make the differentiation. However, while the authors collected data from three octants of reciprocal space, they do not indicate whether they attempted to average them according to $4/mmm$. These intensity data are apparently not available as supplementary material. On the basis of the coordinates resulting from their refinement, the structure should properly be described in space group $I\bar{4}2m$ (Laue symmetry $4/mmm$).

The $I\bar{4}2m$ coordinates, relative to the conventional origin which is displaced by $\Delta y = \frac{1}{2}$, $\Delta z = \frac{1}{4}$ from that used in the $I\bar{4}$ description, are given in Table I. The only coordinate adjustment necessary to achieve the symmetry of $I\bar{4}2m$ is to shift the Se atom by 0.0004 Å so that it lies on a mirror plane; the reported (*1*) e.s.d. in the position

* Contribution No. 7607 from the Arthur Amos Noyes Laboratory of Chemical Physics. This research was supported in part by the National Institutes of Health (GMS-16966-18).

0022-4596/88 $3.00

TABLE I

$ZnIn_2Se_4$: COORDINATES, SPACE GROUP $I\bar{4}2m$

Site	Atom	x	y	z
4d	Zn,In	0	0.5	0.25
2b	Zn,In	0	0	0.5
8i	Se	0.2716	$-x$	0.3846

of the Se atom is considerably larger—about 0.0015 Å. The $I\bar{4}2m$ description emphasizes that the two metal sites labeled "2a" and "2b" in the earlier $I\bar{4}$ description are equivalent by symmetry, that the "2c" site has symmetry $\bar{4}2m$ rather than $\bar{4}$, and that the Se atom lies on a mirror plane.

The only feature of the $I\bar{4}$ structure which deviates significantly from $I\bar{4}2m$ symmetry is the anisotropic "thermal motion" of the selenium atom, as represented by the U_{ij}'s. We have calculated a set of structure factors from the reported positions and U_{ij}'s (*1*), assuming the space group to be $I\bar{4}$. When averaged, this calculated set shows an agreement between equivalent reflections in $4/mmm$ symmetry of 0.025, well within the R value of 0.079 cited (*1*) for the final agreement between F_o and F_c. Thus, one cannot eliminate the higher symmetry space group on the basis of either calculated or observed structure factors.

Two other items support the assignment of the space group as $I\bar{4}2m$: (1) Because of the disorder of the metal atoms, all metal sites contain equivalent atoms. Thus, the selenium atoms are coordinated by atoms arranged with m symmetry, and there is no physical reason for the Se atoms either to be located off the mirror planes or to have U_{ij} values which violate the symmetry of their surroundings. (2) The c/a ratio of the unit cell, 2.007, is consistent with that reported (*3*) for a disordered $I\bar{4}2m$ system (as represented by the β form of $HgGa_2Ti_4$) rather than with the lower c/a values reported for the $I\bar{4}$ systems in which the cations are ordered.

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