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On the Space Group of $Cs_7Cd_3Br_{13}$

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The crystal structure of $Cs_7Cd_3Br_{13}$, recently described as noncentrosymmetric in space group $I\bar{4}c2$, should instead be described as centrosymmetric, space group $I4/mcm$. Other details of the structure are effectively unchanged. © 1993 Academic Press, Inc.

The synthesis and crystal structure of the ternary compound $Cs_7Cd_3Br_{13}$ have recently been reported (*1*). The structure was described and refined in the non-centrosymmetric space group $I\bar{4}c2$ (tetragonal; a = 18.003(2) Å, c = 11.203(3) Å, Z = 4). There seems to be no reason why it should not be described in the centrosymmetric space group $I4/mcm$. Starting coordinates in $I4/mcm$ were obtained from those in Table II of Ref. (*1*) by incrementing y by 0.5, decrementing z by 0.25 (in order to place the origin on a conventional center of symmetry), and, where necessary, slightly shifting an atom to place it on a symmetry element; the largest such shift was about 0.07 Å, for Br(1). Least-squares refinement was based on the 602 "observed" reflections recovered from NAPS Document 04946. At convergence (maximum shift, 0.04σ), R was 0.049 for 38 parameters; for the $I\bar{4}2c$ refinement (*1*), R was 0.046 for 54 parameters. The slight decrease in going to the lower symmetry can easily be blamed on the additional parameters—and especially the anisotropic coefficients U_{ij} for some of the atoms—being able to partially compensate for systematic errors such as absorption. The final $I4/mcm$ parameters are given in Tables I and II. Except for Br(1), as already noted, the revised coordinates differ only trivially from those reported earlier.

TABLE I

COORDINATES, SPACE GROUP $I4/mcm$

Atom	Wyckoff position	Mult.	x	y	z
Cs(1)	h	8	0.2098(2)	0.7098	0.0
Cs(2)	j	16	0.2004(1)	0	0.25
Cs(3)	b	4	0.0	0.5	0.75
Cd(1)	h	8	0.3724(3)	0.8724	0.0
Cd(2)	c	4	0.5	0.5	0.0
Br(1)	l	16	0.3240(3)	0.8240	0.1996(3)
Br(2)	a	4	0.5	0.5	0.25
Br(3)	k	16	0.3439(2)	0.0125(2)	0.0
Br(4)	k	16	0.3896(2)	0.6090(2)	0.0

TABLE II

ANISOTROPIC COEFFICIENTS ($\times 10^4$), SPACE GROUP $I4/mcm$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	234(10)	234(10)	185(14)	−36(9)	0	0
Cs(2)	188(11)	395(12)	323(11)	0	0	−2(12)
Cs(3)	726(24)	726(24)	450(31)	0	0	0
Cd(1)	193(11)	193(11)	232(17)	−50(10)	0	0
Cd(2)	137(13)	137(13)	122(20)	0	0	0
Br(1)	549(15)	549(15)	164(16)	−42(14)	0	0
Br(2)	187(18)	187(18)	139(28)	0	0	0
Br(3)	453(22)	183(20)	654(25)	8(17)	0	0
Br(4)	188(18)	204(18)	322(16)	69(12)	0	0

Note. The form of the displacement factor is $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$.

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The main point of this communication is to point out that the structure is required, by the symmetry of the revised space group, to be centrosymmetric. The original authors elected space group $I\bar{4}2c$ over $4/mcm$ on the basis of the distribution of normalized structure factors, which they found "strongly indicated that the space group is acentric." This distribution (which I have confirmed as favoring the lack of a center) is obviously not to be trusted as an indicator. (Note that, even in the noncentrosymmetric $I\bar{4}2c$ model derived earlier (*1*), the deviations from centrosymmetry are so small as to be negligible in any test of this sort.)

Reference

1. K. D. Sieber, P. S. Bryan, H. R. Luss, J. L. Hobson, B. R. Sever, D. P. Trauernicht, S. A. Ferranti, and L. B. Todd, *J. Solid State Chem.* **100,** 1 (1992).