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Temperature Dependence of Atomic Thermal Parameters of Lead Chalcogenides, PbS, PbSe and PbTe

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Abstract. Thermal parameters of PbX (X = S, Se and Te) have been measured at temperatures ranging from 120 to 298 K by single-crystal X-ray diffraction methods. Crystal data: $M_r = 239{\cdot}25$, 286·15, 334·79; cubic; $Fm3m$; $Z = 4$; Mo $K\alpha_1$; $\lambda = 0{\cdot}70926$ Å; $a =$ 5·9143 (4), 6·1054 (5), 6·4384 (4) Å at 120 K, and $a = 5{\cdot}9315$ (7), 6·1213 (8), 6·4541 (9) Å at 298 K; $\mu = 82$, 90, 74 mm^{-1}; and $F(000) = 378{\cdot}1$, 449·5, 518·5, for PbS, PbSe and PbTe, respectively. Final agreement factors for PbS, PbSe and PbTe are $R = 0{\cdot}050$, 0·029, 0·047 for 698, 403 and 873 reflections at 120 K, and $R = 0{\cdot}050$, 0·029, 0·049 for 689, 770 and 807 reflections at 298 K. The lattice constants of PbS at 150, 200 and 250 K are 5·9181 (3), 5·9237 (3) and 5·9297 (3) Å. Thermal parameters of the Pb atoms are larger than those of the lighter X atoms at 298 K. The ratio $B_{\rm Pb}/B_X$ decreases monotonically with lowering of temperature keeping the relation $B_{\rm Pb}/B_{\rm Te} > B_{\rm Pb}/B_{\rm Se} > B_{\rm Pb}/B_{\rm S}$.

Introduction. Lead chalcogenides (PbX, X = S, Se and Te) have the sodium chloride structure. The thermal parameters of the Pb atoms have been observed to be larger than those of the X atoms, and anharmonic thermal vibration of the Pb atom has been detected in difference syntheses (Noda, Ohba, Sato & Saito, 1983). However, the thermal parameter of the heavier atom is smaller in sodium halides (Buyers & Smith, 1968; Martin & O'Connor, 1978). The temperature dependence of the thermal parameters of these semiconductors has been measured to confirm that the amplitude of the thermal vibration of Pb is larger than those of the lighter chalcogen atoms at room temperature.

Experimental. Rectangular parallelepipeds grown from vapour, 0·05 × 0·08 × 0·09, 0·03 × 0·06 × 0·07 and 0·03 × 0·04 × 0·10 mm for PbS, PbSe and PbTe, respectively. Cell constants refined by least squares for 17 2θ values ($38 < 2\theta < 43°$). X-ray intensity measurements at 120, 150, 200, 250 and 298 K for PbS, and at 120 and 298 K for PbSe and PbTe on a Rigaku AFC-5 four-circle diffractometer at the Institute for Molecular Science, graphite-monochromatized Mo $K\alpha$ radiation. Crystals were cooled by blowing temperature-controlled nitrogen gas. $2\theta_{\max} = 80°$ (h,k $-12\rightarrow12$, l $0\rightarrow12$), θ–2θ scan. No significant decrease of the standard reflections, *ca* 700 non-zero intensities obtained for each measurement, about 50 independent reflections. Corrections for absorption (Busing & Levy, 1967) and thermal diffuse scattering (Stevens, 1974). For example, the transmission factor for PbSe was 0·01–0·09. A scale factor, isotropic thermal parameters and an isotropic secondary-extinction-correction parameter (Zachariasen, 1967) refined with full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). $\sum w||F_o| - |F_c||^2$ minimized, $w^{-1} = \sigma^2(|F_o|) + (0{\cdot}02|F_o|)^2$, $\Delta/\sigma < 0{\cdot}3$. For PbS at 120 K, $R = 0{\cdot}050$, $wR = 0{\cdot}067$, $S = 2{\cdot}48$ for 698 reflections; at 150 K, $R = 0{\cdot}050$, $wR = 0{\cdot}067$, $S = 2{\cdot}28$ for 682 reflections; at 200 K, $R = 0{\cdot}050$, $wR = 0{\cdot}067$, $S = 2{\cdot}17$ for 689 reflections; at 250 K, $R = 0{\cdot}052$, $wR = 0{\cdot}068$, $S = 2{\cdot}10$ for 689 reflections; at 298 K, $R = 0{\cdot}050$, $wR = 0{\cdot}068$, $S = 2{\cdot}59$ for 689 reflections. For PbSe at 120 K, $R = 0{\cdot}029$, $wR = 0{\cdot}033$, $S = 1{\cdot}0$ for 403 reflections; at 298 K, $R = 0{\cdot}029$, $wR = 0{\cdot}030$, $S = 0{\cdot}95$ for 770 reflections. For PbTe at 120 K, $R = 0{\cdot}047$, $wR = 0{\cdot}042$, $S = 1{\cdot}19$ for 873 reflections; at 298 K, R

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Table 1. *Atomic thermal parameters* (Å^2) *obtained by X-ray study*

	PbS		PbSe		PbTe	
Temp. (K)	B_{Pb}	B_S	B_{Pb}	B_{Se}	B_{Pb}	B_{Te}
120	0·54 (2)	0·58 (4)	0·55 (1)	0·49 (1)	0·65 (1)	0·47 (1)
150	0·69 (2)	0·71 (4)				
200	0·88 (2)	0·89 (5)				
250	1·08 (2)	1·04 (5)				
298	1·29 (2)	1·23 (4)	1·34 (1)	1·07 (1)	1·61 (2)	1·11 (1)
293–301*	1·283 (3)	1·247 (11)	1·427 (3)	1·130 (4)	1·781 (5)	1·228 (4)

* Results of Noda, Ohba, Sato & Saito (1983) using Ag *K*α radiation at 293, 295 and 301 K for PbS, PbSe and PbTe, respectively.

$= 0·049$, $wR = 0·044$, $S = 1·38$ for 807 reflections. After averaging the equivalent reflections ($0·026 < R_{int} < 0·049$), the final R value was 0·010 to 0·021 for 53–66 unique reflections.* Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. As seen from Table 1, the ratio B_{Pb}/B_S decreases monotonically with lowering of temperature. Though not significant, the thermal parameter of Pb is slightly smaller than that of S below 200 K. However, the thermal vibration of Pb is still larger than those of Se and Te at 120 K. The larger mean-square displacement of the heavier ion was also observed in AgCl (Vijayaraghavan, Nicklow, Smith & Wilkinson, 1970) and $Pb(NO_3)_2$ (Kulkarni & Bichile, 1975). The reason for this phenomenon may be related to the partially covalent character of the chemical bonds and a high degree of anharmonicity. However, a clear-cut interpretation has not been obtained yet, although the lattice dynamics of PbS (Elcombe, 1967), PbTe (Cochran, Cowley, Dolling & Elcombe, 1966), AgCl (Vijayaraghavan *et al.*, 1970) and AgBr (Fujii, Hoshino, Sakuragi, Kanzaki, Lynn & Shirane, 1977) have been investigated by neutron inelastic scattering. It is noted that Vijayaraghavan *et al.* (1970) calculated the temperature dependence of thermal parameters to show the larger mean-square displacement for Ag in AgCl above 100 K based on a 13-parameter shell model. Compared with the previous results at room temperature using Ag *K*α radiation (Noda *et al.*, 1983), the thermal parameters of PbS are almost equal; however, those of PbSe and PbTe are smaller by 6 and 11%, respectively. This may be partly due to the large correlation between the thermal parameters and the extinction-correction parameter. The smallest extinction factors (F_o^2/F_c^2) are 0·8, 0·6 and 0·5 for PbS, PbSe and PbTe, respectively.

In order to determine the thermal parameters, single-crystal and powder neutron diffraction experiments were also performed at the Research Reactor Institute, Kyoto University. The powder diffraction pattern was recorded for PbS at room temperature by the θ–2θ step-scan technique and was analyzed on the basis of Rietveld's profile fitting method (Rietveld, 1969): $B_{Pb} = 1·1$ (1), $B_S = 1·0$ (3) Å^2 with $R = 0·094$ for 18 independent reflections.* On the other hand, unreasonable thermal parameters were obtained by single-crystal neutron diffraction methods. The measurements for PbTe at 16, 77 and 300 K were performed on a four-circle diffractometer: $R(F) = 0·024$, $wR = 0·031$ for 23 unique reflections at 300 K.* The thermal parameters plotted against the temperature do not lie on a straight line passing through the origin as shown in Fig. 1. This can be attributed to the large divergence of the diffracted neutron beam from the melt-grown PbTe crystal of poor quality. The relative magnitudes indicate that the thermal vibration of Pb is still larger than that of Te at 77 K, and is nearly equal to that of Te at 16 K.

Lead chalcogenides are employed in optical fiber transmission and pollution monitoring of injection lasers. A loss of the laser generally results from carrier scattering (Casey & Panish, 1978), which is predominantly caused by lattice vibration (Ravich, Efimova & Smirnov, 1970). The root-mean-square amplitudes of the thermal vibration listed in Table 2 are more than 1·4% of a at 120 K and rise to 2·1% at 298 K, while those in GaAs at room temperature remain comparable to those in PbX at 120 K. With respect to the carrier-scattering loss by lattice vibration, the most favorable compound is PbS among the lead chalcogenides.

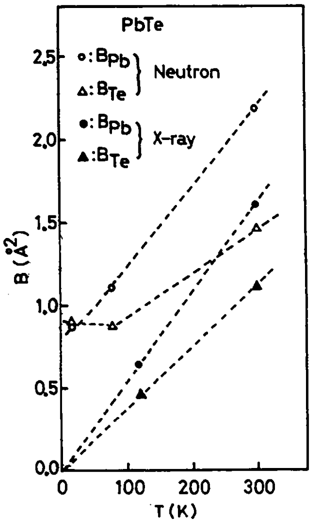

Fig. 1. The temperature dependence of isotropic thermal parameters for Pb and Te atoms in PbTe.

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* Lists of structure factors and details of neutron measurement of PbTe have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43902 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

Table 2. *Root-mean-square displacement* (Å) *of thermal vibration*

Root-mean-square displacements obtained from $\langle u^2\rangle^{1/2} = (1/8\pi^2)^{1/2}B^{1/2}$.

	$\langle u^2\rangle^{1/2}$ at 120 K		$\langle u^2\rangle^{1/2}$ at 298 K		$(\langle u^2\rangle^{1/2}_{298} - \langle u^2\rangle^{1/2}_{120})/a \times 100$ (%)	
	Pb	*X*	Pb	*X*	Pb	*X*
PbS	0·083 (2)	0·086 (3)	0·128 (1)	0·126 (2)	0·76 (5)	0·66 (8)
PbSe	0·083 (1)	0·078 (1)	0·130 (1)	0·116 (1)	0·77 (3)	0·62 (3)
PbTe	0·091 (1)	0·077 (1)	0·143 (1)	0·119 (1)	0·81 (3)	0·65 (3)
GaAs*	(a = 5·654 Å)		0·096	0·087	(at room temperature)	

* Pietsch (1981).

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Structure of Ammonium *catena*-Diammine-di-μ-chromato-cuprate(II), a Compound with Bridging Chromate Groups

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Abstract. $(NH_4)_2[Cu(CrO_4)_2(NH_3)_2]$, $M_r = 365{\cdot}67$, triclinic, $P\bar{1}$, $a = 7{\cdot}362\,(2)$, $b = 6{\cdot}932\,(1)$, $c = 5{\cdot}895\,(1)$ Å, $\alpha = 112{\cdot}39\,(3)$, $\beta = 92{\cdot}79\,(2)$, $\gamma = 107{\cdot}06\,(3)°$, $V = 261{\cdot}5$ Å^3, $Z = 1$, $D_m = 2{\cdot}34\,(5)$, $D_x = 2{\cdot}32$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 4{\cdot}02$ mm^{-1}, $F(000) = 183$, $T = 293$ K. Final $R = 0{\cdot}025$ for 1896 counter reflections. The structure consists of infinite anion chains, parallel to the c axis, in which octahedral copper(II) ions (site symmetry C_i) are linked by two bridging chromium(VI) tetrahedra. The copper(II) octahedron comprises two ammonia molecules [Cu—N 1·972 (2) Å] and four chromate O atoms [Cu—O 2·022 (2) and 2·425 (1) Å, Cr—O ranges from 1·636 (1) to 1·686 (1) Å]. The anion chains are linked through hydrogen bonding from the ammonium cations.

Introduction. An undergraduate project involving the coprecipitation of copper and chromium in salts suitable for thermal decomposition into cupric chromite ($CuCr_2O_4$), led to the production of crystals thought to be $(NH_4)_2[Cu(CrO_4)_2(NH_3)_2]$. Measurement of the unit-cell dimensions indicated that these differed considerably from those of the analogous zinc compound, $(NH_4)_2[Zn(CrO_4)_2(NH_3)_2]$ [$a = 12{\cdot}85\,(2)$, $b = 5{\cdot}912\,(8)$, $c = 7{\cdot}434\,(8)$ Å, $\beta = 111{\cdot}2\,(2)°$, monoclinic (Harel, Knobler & McCullough, 1969)]. As a result of these observations the structure of the title compound was determined.

Experimental. The compound was prepared by the method used for the Zn compound (see above) and an orange prismatic crystal (~0·23 × 0·13 × 0·20 mm)

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