JOURNAL OF MATERIALS SCIENCE 22 (1987) 1657–1662

Debye–Waller parameters of lead sulphide powders

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The Debye–Waller parameters, the effective value B_{eff}, the dynamic component B_d and the static component B_s, of lead sulphide powders with different particle sizes were determined for the bulk and for each constituent atom, lead and sulphur. The effective values for each atom, B_{eff}(Pb) and B_{eff}(S), were linearly related to that for the bulk, B_{eff}(PbS). The effective value and the dynamic component for the bulk, B_{eff}(PbS) and B_d(PbS), were almost equal to those for lead, B_{eff}(Pb) and B_d(Pb), suggesting a small contribution of sulphur atoms to Debye–Waller parameters for the bulk. The mean square displacement of the bulk, $\langle u^2 \rangle_{\text{PbS}}$, was expressed by the atomic mass averaged mean square displacements $\langle u^2 \rangle_{\text{Pb}}$ and $\langle u^2 \rangle_{\text{S}}$ in PbS crystal. The Debye temperature θ_D calculated from B_d(PbS) increased with the decrease in B_s(PbS), and was extrapolated to the θ_D-value of the single crystal at $B_s(\text{PbS}) = 0$. A similar relation between θ_D and B_s were found for lead atom, where θ_D(Pb) was a little bit smaller than θ_D(PbS).

1. Introduction

In the previous papers [1–3], the effective Debye–Waller parameter was discussed by using an assumption of linear combination of two components, dynamic component B_d due to thermal vibration of constituent atoms and static component B_s probably due to the static displacement of atoms associated with various defects. We have successfully determined these two components, B_d and B_s, from the effective values of Debye–Waller parameter, B_{eff}, of isotropic palladium metal powders with different particle sizes [1], anisotropic carbon materials with different origins and heat treatment temperatures [2], and different diatomic crystals with NaCl- and zinc blende-type structures [3].

Metzger *et al.* [4] reported the increase of Debye–Waller parameter with doping hydrogen into a neobidium single crystal. They explained this increase as the atomic displacement due to interstitial hydrogen and call it static Debye–Waller factor.

In different diatomic crystals, the dynamic component B_d of bulk crystals was found to be expressed by a mass-averaged B_d of the constituent atoms [3]. This result might be important to understand the thermal behaviours of bulk crystals from those on the constituent atoms. X-ray diffraction techniques through the determination of effective Debye–Waller parameters has an advantage to obtain the information both on the bulk crystal and on its constituent atoms. In addition, we have shown experimentally that the Debye–Waller parameters depend strongly on the physical state of the sample crystals [1–3, 5–7].

In the present work, the values of effective Debye–Waller parameter, B_{eff}, and its dynamic and static components, B_d and B_s, were determined on the constituent atoms, lead and sulphur, and also on the bulk crystal of lead sulphide powders which were in different physical states. The relations among the B-values were discussed.

2. Experimental details

Lead sulphide powders were prepared by precipitation from NaOH aqueous solution of lead nitrate $Pb(NO_3)_2$ and the aqueous solution of thiourea $(NH_2)_2CS$. Either by changing the concentration of the solutions and the precipitating temperature (40 to 80° C) or by grinding in different periods, the eight powder samples with different B_{eff}-values were obtained. Lead sulphide was selected as the sample because of the NaCl-type crystal structure, ease of preparation, stability in air, and also of only slight deviation from stoichiometry ($10^{-3} \sim 10^{-5}$) [8].

Ten diffraction lines, five pairs of the lines with all even and all odd indices, were chosen in a $\sin^2\theta/\lambda^2$ range of 0.0002 to 0.0031 nm^2. On each line, the integrated intensity was determined by summing up the diffraction intensities measured in every 0.05° step in 2θ by fixed time (40 sec) method and by subtracting the background intensity. Cu$K\alpha$ radiation filtered by nickel foil and a scintillation counter with pulse height analyser were employed. Diffraction intensity measurement was conducted in vacuum at 290 and 79 K.

The effective Debye–Waller parameters for lead and sulphur, B_{eff}(Pb) and B_{eff}(S), are obtained by using the equations;

$$\ln[\{Q(\text{even}) + Q(\text{odd})\}/2f_{\text{Pb}}] = \ln K - B_{\text{eff}}(\text{Pb}) \sin^2\theta/\lambda^2 \quad (1\text{a})$$

and

$$\ln[\{Q(\text{even}) - Q(\text{odd})\}/2f_{\text{S}}] = \ln K - B_{\text{eff}}(\text{S}) \sin^2\theta/\lambda^2 \quad (1\text{b})$$

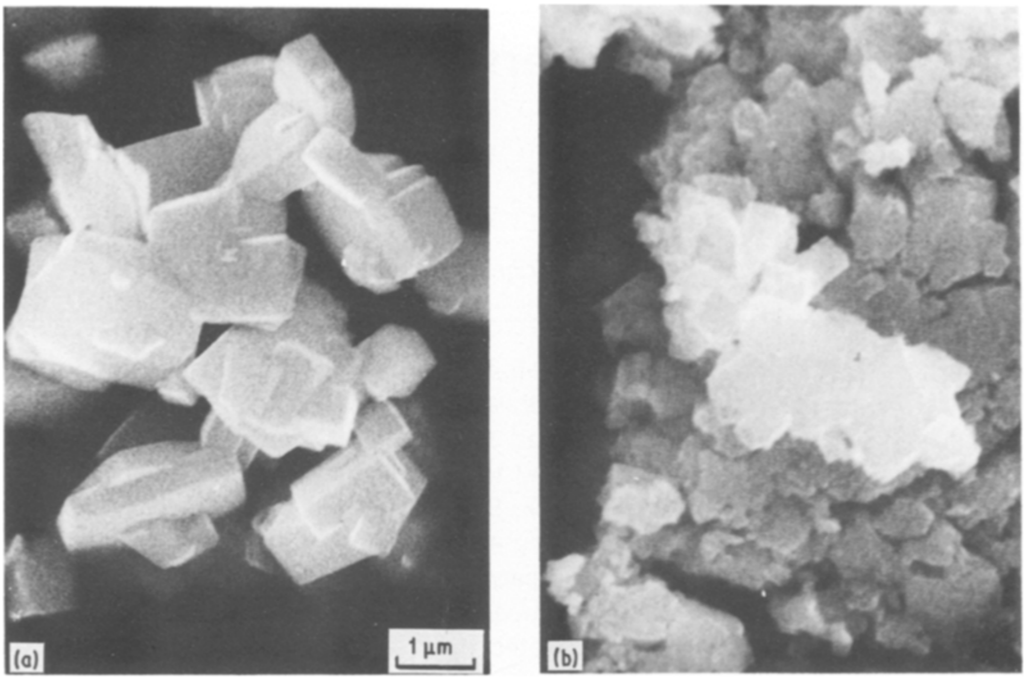

Figure 1 SEM micrographs of lead sulphide powders (a) Sample 4, (b) Sample 5.

where use has been made of a formula

$$Q = \frac{I_{\rm obs}}{pALP} \qquad (2)$$

The detailed experimental procedure of analysis was reported in previous papers [3, 7].

The $B_{\rm eff}$-value for the bulk PbS, $B_{\rm eff}$(PbS), was also determined from the slope of the plot of $\ln [I_{\rm obs}(h\,k\,l)/I_{\rm calc}(h\,k\,l)]$ against $\sin^2\theta/\lambda^2$ through the following equation,

$$\ln [I_{\rm obs}(h\,k\,l)/I_{\rm calc}(h\,k\,l)] = \ln k - 2B_{\rm eff}({\rm PbS})\sin^2\theta/\lambda^2. \qquad (3)$$

Absorption factor A required for the calculation of Q-values and $I_{\rm calc}(h\,k\,l)$, was constant over the experimental range of $\sin^2\theta/\lambda^2$ because of high mass absorption coefficient ($213\,{\rm cm^2\,g^{-1}}$) and thick specimen (1 mm).

The $B_{\rm eff}$-values thus determined at 290 and 79 K were divided into the dynamic and static components, $B_{\rm d}$ and $B_{\rm s}$, through the same procedure as reported previously [1].

3. Results

Fig. 1 shows SEM micrographs of the Samples 4 and 5, which have quite different $B_{\rm eff}$-values (for example, $B_{\rm eff}({\rm PbS}) = 0.0056$ and $0.0130\,{\rm nm^2}$ at 79 K, respectively). The particles of Sample 4 are plate-shaped (2 to 3 μm wide and about 0.5 μm thick), while Sample 5 consists of much smaller and irregularly shaped particles.

In Fig. 2a, the plots of $\ln [\{Q({\rm even}) \pm Q({\rm odd})\}/2f]$ against $\sin^2\theta/\lambda^2$ are shown, as an example, of which the slopes give $B_{\rm eff}$- values for lead and sulphur. The experimental points of $\ln [\{Q({\rm even}) + Q({\rm odd})\}/2f_{\rm Pb}]$ for lead are less scattered than those of $\ln [\{Q({\rm even}) - Q({\rm odd})\}/2f_{\rm S}]$ for sulphur. Therefore, the straight line for lead was firstly determined in Fig. 2a and then the line for sulphur was determined so as to give the same intercept K at $\sin^2\theta/\lambda^2 = 0$. The accuracy in $B_{\rm eff}$(Pb) was about $\pm 0.0002\,{\rm nm^2}$, but that in $B_{\rm eff}$(S) was much larger, $\pm 0.0005\,{\rm nm^2}$.

In Fig. 2b, the plots of $\ln [I_{\rm obs}(h\,k\,l)/I_{\rm calc}(h\,k\,l)]$ against $\sin^2\theta/\lambda^2$ are shown, of which the slope gives $B_{\rm eff}$-value for the bulk PbS, $B_{\rm eff}$(PbS). Two linear relations are obtained for the diffraction lines with all even indices and with all odd indices. These two linear relations are parallel and give the same $B_{\rm eff}$-values. The accuracy in $B_{\rm eff}$(PbS) was estimated to be $\pm 0.0004\,{\rm nm^2}$.

From the $B_{\rm eff}$-values at 79 and 290 K, the Debye temperature $\theta_{\rm D}$ and two components, $B_{\rm d}$ and $B_{\rm s}$, were evaluated. The accuracies in $\theta_{\rm D}$ for lead and also for PbS were ±6 to 9 K and those in $B_{\rm d}$ and $B_{\rm s}$ ± 0.0004 to $0.0007\,{\rm nm^2}$. Those of $\theta_{\rm D}$, $B_{\rm d}$ and $B_{\rm s}$ for sulphur were much larger, about ±20 K and $\pm 0.0008\,{\rm nm^2}$, respectively, because of low accuracy in estimating $B_{\rm eff}$(S)-value. The results on eight samples are listed in Table I.

4. Discussion

4.1. Effective values of Debye–Waller parameters

In Fig. 3, $B_{\rm eff}$(Pb) and $B_{\rm eff}$(S) are plotted against $B_{\rm eff}$(PbS). The relations for $B_{\rm eff}$(Pb) and for $B_{\rm eff}$(S) are linear through the origin, independent of temperature of measurement. Here, two points must be noted; lead atoms have much larger value of $B_{\rm eff}$ than sulphur atoms, being about 2.2 times larger, and the $B_{\rm eff}$-value for the bulk PbS, $B_{\rm eff}$(PbS), practically equals that for lead. These results suggest a small contribution of S atoms to the effective value of Debye–Waller parameter.

In Fig. 4, the $B_{\rm d}$-values for each atom and the bulk crystal are plotted as a function of the corresponding $B_{\rm eff}$-values. The relation depends on temperature of

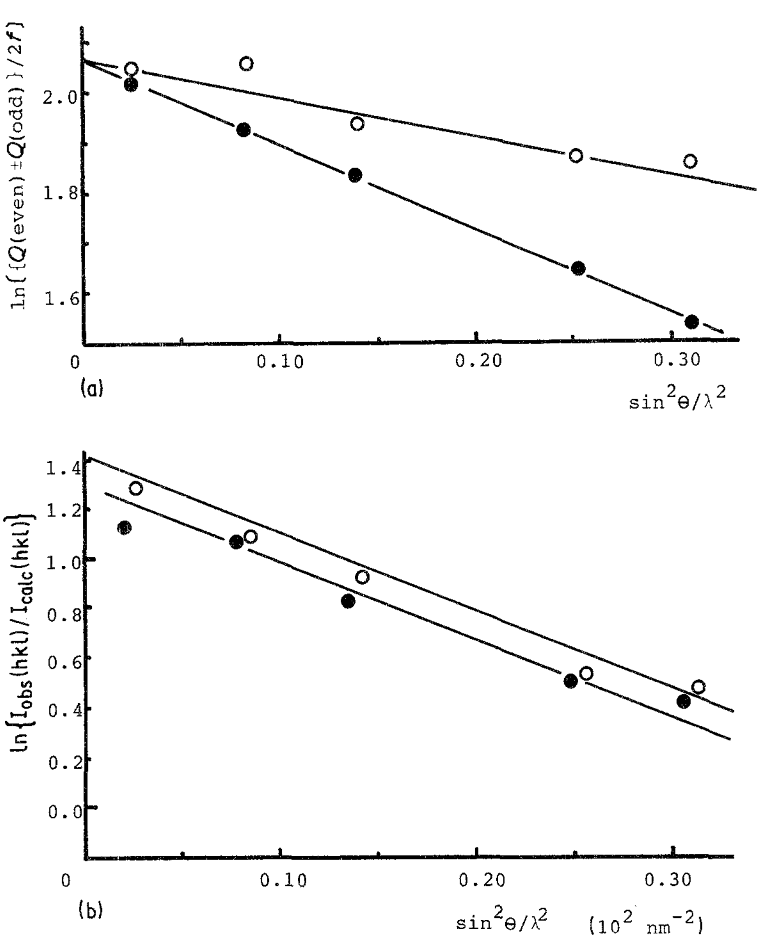

Figure 2 Determination of effective Debye–Waller parameters at 290 K. (a) B_{eff}(Pb) and B_{eff}(S), (b) B_{eff}(PbS).

measurement and seems to be in common with lead, sulphur and even the bulk PbS, though the experimental points for sulphur are scattered. As shown in the figure, the difference between the line for $B_{\text{d}} = B_{\text{eff}}$ and the experimental curve yields the static component B_{s}. The increase in B_{eff}-value results from the increase in both dynamic and static components, but the higher the B_{eff}-value, the larger the contribution of B_{s} since the B_{d}-value tends to saturate at larger B_{eff}-values. The similar relation between B_{eff} and B_{d} has been observed on palladium metal powders [1]. In addition, it is worth noting that the static component B_{s} is independent of temperature as can be proved by the lines connecting two experimental points at 290 and 79 K in Fig. 4 for each specimen, which are parallel to the line $B_{\text{d}} = B_{\text{eff}}$.

4.2. Dynamic component in Debye–Waller parameter

Fig. 5 shows the linear relations between B_{d}-values for

TABLE I Experimental results on PbS

Sample	T (K)	Pb				S				PbS			
		B_{eff}	B_{d}	θ_{D}	B_{s}	B_{eff}	B_{d}	θ_{D}	B_{s}	B_{eff}	B_{d}	θ_{D}	B_{s}
1	79	0.80	0.36	113	0.44	0.42	0.20	500	0.22	0.78	0.36	152	0.42
	290	1.69	1.25			0.65	0.43			1.64	1.22		
2	79	1.42	0.46	99	0.96	0.95	0.51	266	0.44	1.40	0.48	130	0.92
	290	2.60	1.64			1.94	1.50			2.57	1.65		
3	79	0.73	0.39	109	0.34	0.31	0.31	370	0.0	0.77	0.34	158	0.43
	290	1.70	1.36			0.80	0.80			1.58	1.15		
4	79	0.53	0.31	123	0.22	0.22	0.22	455	0.0	0.56	0.29	173	0.27
	197	0.95	0.73			0.44	0.44			0.89	0.62		
	294	1.31	1.09			0.60	0.60			1.23	0.96		
5	79	1.51	0.41	105	1.10	0.69	0.30	385	0.39	1.30	0.43	142	0.89
	300	2.60	1.50			1.17	0.78			2.34	1.47		
6	79	0.52	0.23	144	0.29	0.19	0.19	538	0.0	0.50	0.23	192	0.27
	290	1.07	0.78			0.39	0.39			1.02	0.75		
7	79	0.93	0.41	106	0.52	0.39	0.39	328	0.0	0.97	0.46	133	0.51
	290	1.96	1.44			0.99	0.99			2.10	1.59		
8	79	1.08	0.45	101	0.63	0.67	0.28	404	0.39	1.13	0.46	133	0.67
	290	2.22	1.59			1.06	0.67			2.25	1.58		

T, temperature of measurement, B_{s}, in $10^{-2}\,\text{nm}^2$ θ_{D} (K).

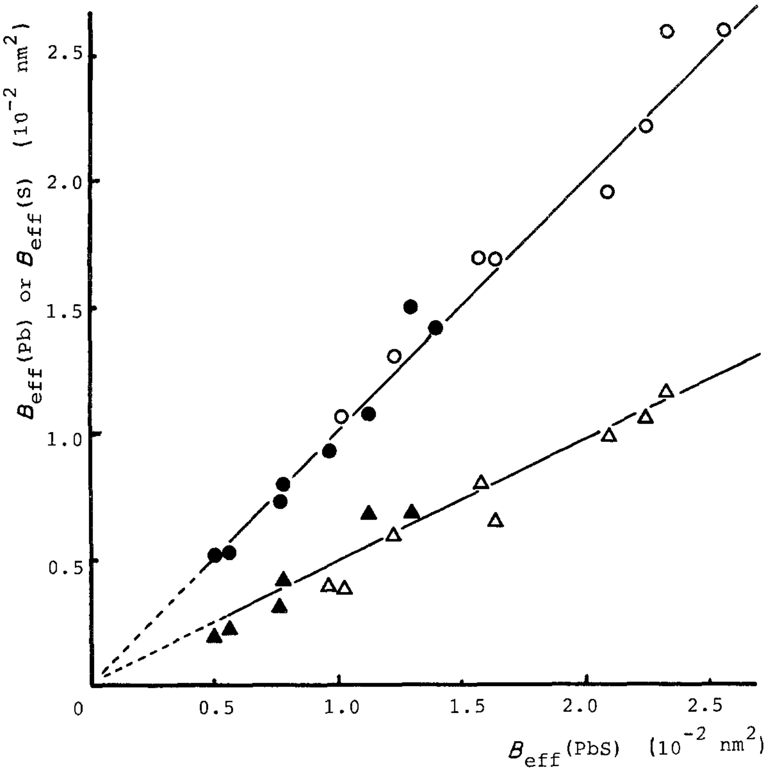

Figure 3 Relations of effective value B_{eff} for lead and sulphur to that for the bulk PbS; B_{eff}(Pb): (○) 290 K (●) 79 K: B_{eff}(S): (△) 290 K (▲) 79 K.

each atom and that for the bulk, like as found in Fig. 3. The dynamic component for the bulk, B_d(PbS), equals that for lead, B_d(Pb), and the value of B_d(Pb) is roughly twice that of B_d(S).

The dynamic component B_d is related to the mean square thermal displacement $\langle u^2 \rangle$ of constituent atoms;

$$B_d = (8\pi^2/3)\langle u^2 \rangle \qquad (4)$$

from which the mean square displacement $\langle u^2 \rangle_{Pb}$, $\langle u^2 \rangle_S$ and $\langle u^2 \rangle_{PbS}$ for each atom and the bulk were determined. When the mean square displacement for the bulk crystal was calculated by the following equation:

$$\langle u^2 \rangle_{calc} = \{m_{Pb}/(m_{Pb} + m_S)\}\langle u^2 \rangle_{Pb} + \{m_S/(m_{Pb} + m_S)\}\langle u^2 \rangle_S \qquad (5)$$

a good agreement with the observed displacement $\langle u^2 \rangle_{PbS}$ was obtained, as shown in Fig. 6, where m_{Pb} and m_S are atomic masses of respective atom.

In Fig. 7, the Debye temperature θ_D which is calculated from B_d-value is shown as a function of B_s. On the bulk crystal, θ_D decreases gradually with the increase in B_s. On a single crystal of PbS, the Debye temperatures of 225 and 229 K were reported from specific heat and elastic constants, respectively. The θ_D

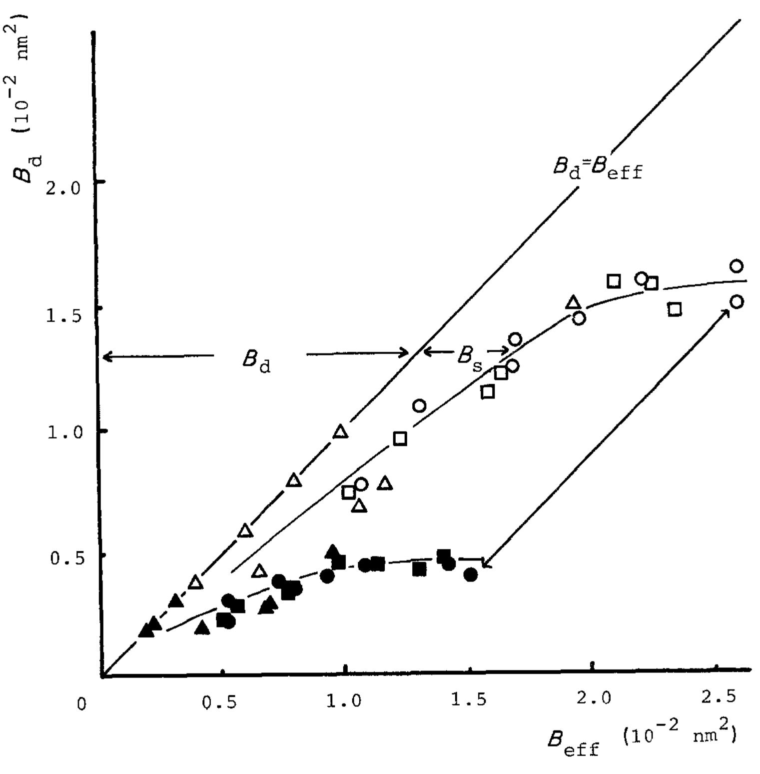

Figure 4 Relations between dynamic component B_d and effective value B_{eff} for lead (○) 290 K (●) 79 K; sulphur (△) 290 K (▲) 79 K; and the bulk PbS: (□) 290 K (■) 79 K.

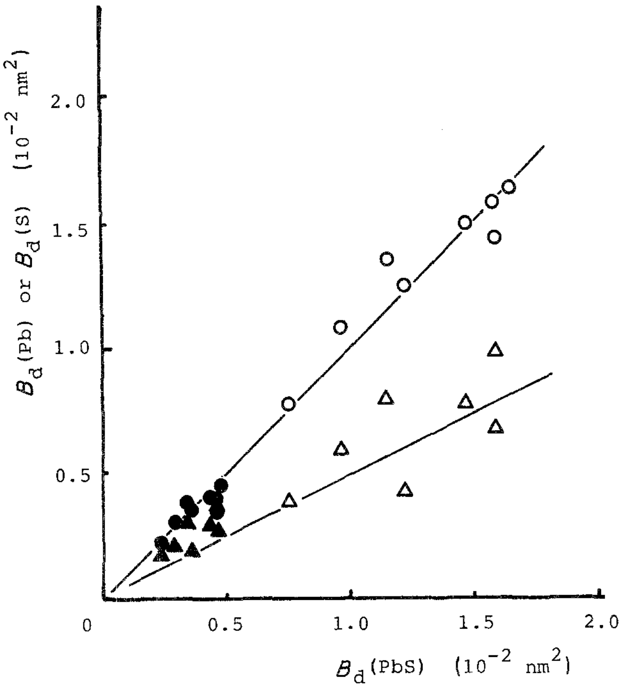

Figure 5 Relations of dynamic components B_d for lead (○) 290 K (●) 79 K and sulphur (△) 290 K, (▲) 79 K to that for the bulk PbS.

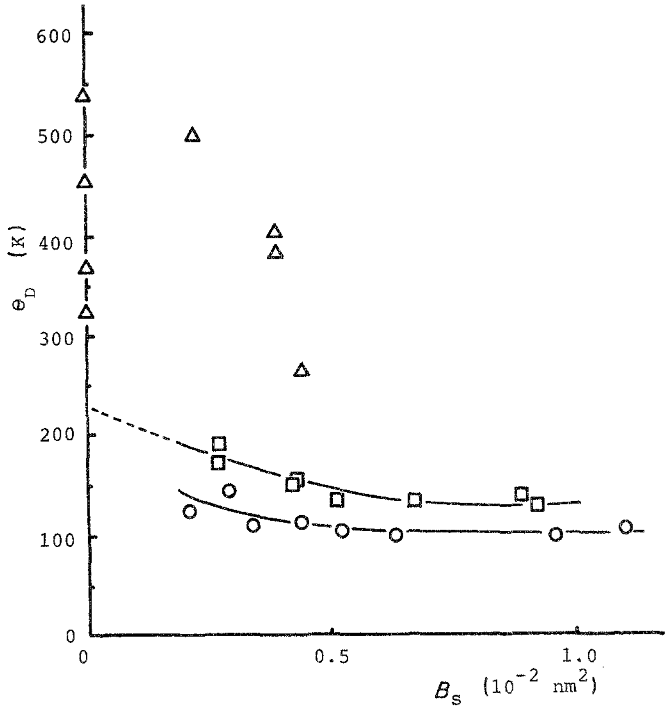

Figure 7 Relations between Debye temperature θ_D and static component B_s. (□) PbS; (○) Pb; (△) S.

against B_s relation in Fig. 7 seems to be extrapolated to the reported temperature at $B_s = 0$, which corresponds to a perfect single crystal. The similar results were previously found for palladium metal powders [1] and for graphite [2].

A similar dependence of θ_D on B_s is found for lead atom, but the value of θ_D is a little smaller than that for the bulk crystal. The extrapolated θ_D-value to $B_s = 0$, however, seems to be much higher than the Debye temperature for lead metal (85 K). It is probably reasonable because Pb–S bonding in PbS is much stronger than Pb–Pb bonding in metal. The experimental points for sulphur scatter so much that the dependence of θ_D on B_s can not be discussed. However, it can be concluded that sulphur atoms have much higher Debye temperature than lead atoms.

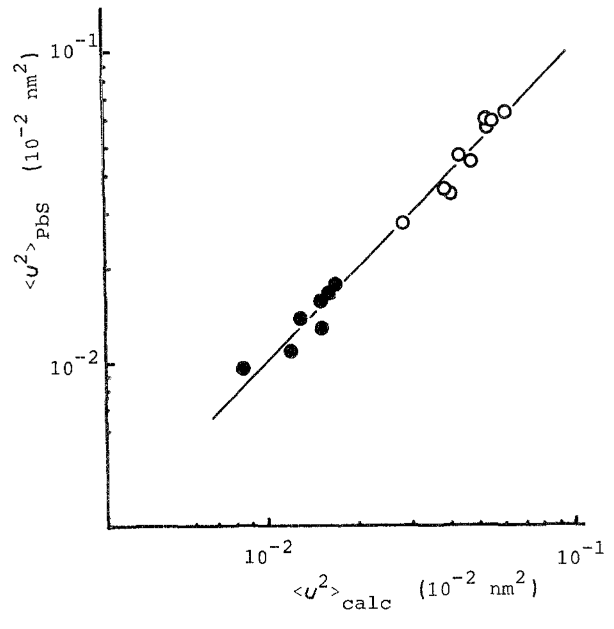

Figure 6 Relation between mean square displacement for the bulk crystal observed $\langle u^2 \rangle_{PbS}$ and that calculated $\langle u^2 \rangle_{calc}$ (Equation 6). (●) 79 K, (○) 290 K.

4.3. Static component in Debye–Waller parameter

On a single crystal of neobidium, it was shown experimentally that static Debye–Waller parameter increases proportionally with the concentration of interstitial hydrogen atoms, i.e., the concentration of defects [4]. In the present work, the value of static component B_s shows qualitative correspondence with morphology of the particles. As shown in Fig. 1, for example, Sample 4 (Fig. 1a) is well crystallized and has a very low value (0.0027 nm^2) of B_s(PbS), and Sample 5 (Fig. 1b) is poorly crystallized and has relatively high value (0.0089 nm^2) of B_s(PbS). So, the static component B_s depends not only upon the structural defects, such as point defects, but also upon the defects in a wide-meaning, such as grain boundaries and surface.

In Fig. 8, B_s is plotted against B_{eff}. As expected from the relation of B_d against B_{eff} in Fig. 4, the ratio B_s/B_{eff} increases with the increase in B_{eff}; at 290 K about 20% at $B_{eff} = 0.01\ nm^2$ and about 40% at $B_{eff} = 0.025\ nm^2$. This suggests the importance of B_s in the effective value of Debye–Waller parameter. If we ignore the B_s component, we may bring up wrong conclusions on thermal vibration of atoms as well as on Debye temperature, particularly for fine powders. Subhadra and Sirdeshmukh [9] determined the overall value of Debye–Waller parameter on various chalcogenides, including PbS, and calculated the Debye temperature ignoring the static component and the difference in B-value for constituent atoms.

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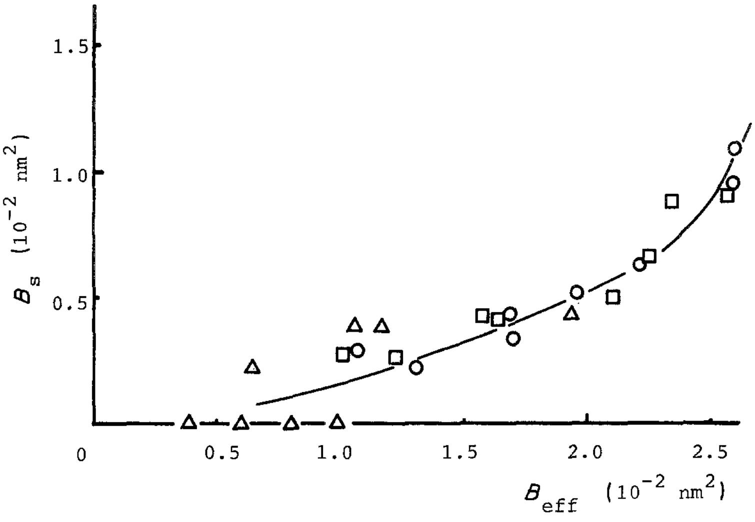

Figure 8 Relations between B_s and B_{eff}. PbS (□); Pb (○); S (△).

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Received 5 June
and accepted 9 September 1986