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Microhardness of as-grown and annealed lead sulphide crystals

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The results of the measurement of Vickers microhardness of {1 0 0} faces of synthetic lead sulphide crystals are reported. It was found that, for loads lower than ~60 g, the microhardness value depends on the applied load, the duration of indentation, and on the density of dislocations in the crystals, but that at higher loads the microhardness is independent of the applied load and is dependent on the dislocation density in the crystals. Furthermore, an influence of the adsorption of water on the microhardness of the crystals was observed. The observations are discussed in terms of the existence of a distorted zone near the crystal–medium interface, a concept originally advanced by Berzina *et al.* Finally, this concept of the distorted zone is briefly compared with more recent approaches of microhardness.

1. Introduction

Indentation hardness at low loads is an evasive property of crystalline solids as it is often found that there is a considerable disagreement among the results obtained by different workers [1–3]. Confusion always exists regarding the variation of hardness number with load and duration of indentation [1–9]. In the case of Vickers microhardness determination, the important factors that influence the microhardness value at low loads are the load determination, the impression measurement and the nature of the material under study [1–3]. The first two factors are instrumental in origin while the third is associated with the compositional and deformation properties of the material under investigation.

During the last few years, a number of papers have appeared on the variation of microhardness of different crystals with loads [4–6, 8–15]. In several cases it was found [4–6, 8] that, with an increase in load, initially the microhardness increases up to a particular value of load, then slowly decreases and finally becomes constant. This observation has been explained in terms of the existence of a distorted zone of the crystal surface. The concept of the distorted zone was first advanced in 1965 by Berzina *et al.* [4] and later in 1971 adopted by the present author for PbS crystals [16]. Unfortunately, the original paper on the concept of the distorted zone was not remembered in the above works [11, 13–15] nor was the work on PbS crystals published.

This paper reports the unpublished experimental results on the change of Vickers microhardness of synthetic PbS crystals with load and duration of indentation. It also describes the effect of the density of defects present in the crystals on the value of their microhardness.

2. Experimental details

A large synthetic lead sulphide crystal, grown from the melt by the Bridgman method and kindly supplied by Dr R. Thyagarajan, was used for experimental purposes. It was cleaved into rectangular blocks of about 3 mm × 5 mm × 5 mm dimensions. Annealing of these blocks was then carried out in the air in a silica crucible kept in a muffle furnace at different temperatures for a period of 4 h. This annealing duration was selected on the basis of our previous experiments [17] in which it was found that after about 75 min the dislocation density in natural crystals attains a constant value of about $6 \times 10^6\,\mathrm{cm}^{-2}$. Subsequently, the samples were brought to room temperature either by switching off the furnace or by quenching them in the air or in cold tap water. Cleavages of these untreated, annealed and quenched crystals were subjected to hardness tests with a Vickers projection microscope. To reveal the dislocation structure of the crystals, a solution of 2 parts concentrated HCl and 1 part thiourea aqueous solution saturated at 25° C or 1 part aqueous solution of 1 N NH_4Cl [17–19] was used.

To study the dependence of microhardness on load, the length, d (in μm), of the diagonal of the indentation impression obtained after applying loads, P (g), varying from 2 to 150 g for 15 sec was measured. The length of the indentation rosette ray, l, which is the distance from the part of the termination of dislocations set in motion by the indentor on one side of the impression to the other along the $\langle 1 0 0 \rangle$ directions, was also measured for these loads. From these measurments, the Vickers hardness number, $H_v = 1.854P/d^2$ and, in analogy with it, a stress parameter P/l^2 was calculated.

It has been reported [3, 20] that the microhardness of PbS is anisotropic. During the present work, however, it was found that, on the cleavage face of an unannealed crystal, the value of microhardness is practically independent of the orientation of the indentor. Despite this observation, in all the measurements the indentor was so arranged every time that the

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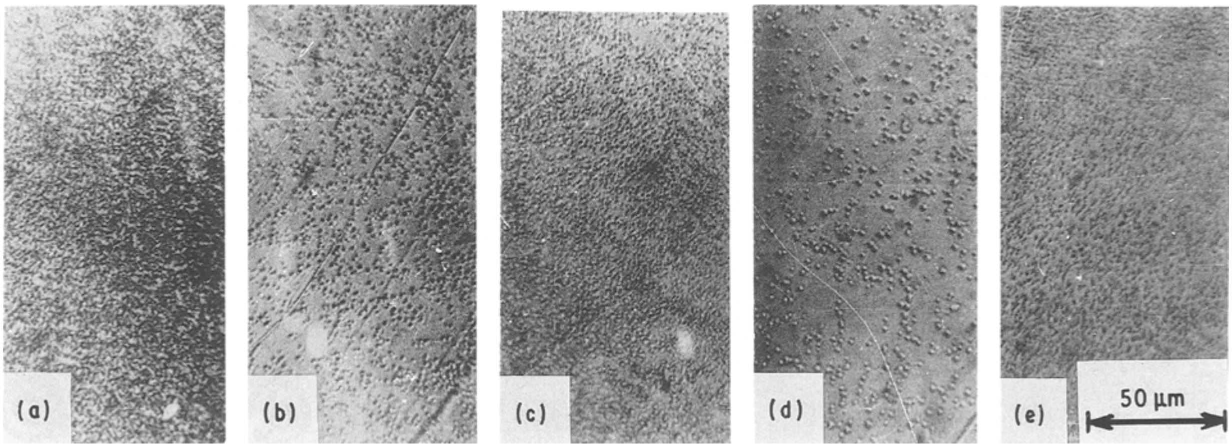

Figure 1 Etch-pit patterns on the (1 0 0) face of lead sulphide crystals subjected to different thermal treatments: (a) untreated, (b) heated at 480° C and air quenched, (c) heated at 570° C and air quenched, (d) annealed at 750° C and slowly cooled down to room temperature, and (e) heated at 750° C and quenched in water. Duration of heating for all samples = 4 h.

diagonal of the impression always made an angle of 62° with the ⟨1 0 0⟩ edges of the crystal samples.

In another related series of experiments the effect of water adsorption on the nature of the hardness against load curves was studied. For this purpose, a cleavage face of an untreated crystal was kept in water for 70 h (wet conditions), while its counterpart was kept in a closed vessel containing P_2O_5 for the same period (dry conditions); microhardness indentations were then made for 15 sec.

In order to investigate the dependence of microhardness of the crystals on the time of loading, measurements were made at a load of 20 g on a pair of matched cleavage faces one of which was kept in wet conditions while its counterpart was kept in dry conditions. Measurements were also made for some samples immediately after cleaving and after keeping the cleavage face in the air for a long time.

3. Experimental results

The etch-pit patterns on the cleavage faces of the crystals subjected to different thermal treatments are shown in Fig. 1. It may be observed that, as reported in a previous paper on natural lead sulphide crystals [17], the dislocation density decreases upon the annealing of the crystals. Moreover, the dislocation density decreases in samples quenched from 480° C while it increases for samples quenched from 570 and 750° C. Also the dislocation density in crystals annealed at 750° C and quenched from 480° C is nearly the same. The value of dislocation density, ϱ, estimated by counting the number of etch pits in randomly selected areas, and the type of thermal treatment given to the corresponding samples are given in Table I.

The dependence of microhardness of crystals under wet and dry conditions on the time of loading is illustrated in Fig. 2. It is obvious that the hardness of the crystals under dry conditions is constant while that of the crystals under wet conditions decreases with an increase in the duration of indentation. It was also found that the curves of the time dependence of microhardness were of the upper and lower types in Fig. 2 for cleavages which were freshly obtained and for those where measurements were made a long time after cleaving, e.g. after several days, respectively.

The load dependence of microhardness is shown in Fig. 3 for untreated, annealed and quenched crystals. Obviously, with an increase in load, H_v increases and then, except for samples annealed at 750° C and for those quenched from 480° C, it attains a constant value after passing through a maximum value at a load of about 60 g. The values of maximum hardness, H_{max}, and constant microhardness, H_{const}, for various samples are given in Table I.

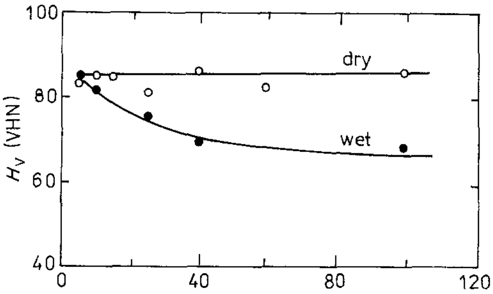

Figure 2 Dependence of microhardness of the (1 0 0) face of thermally untreated PbS crystals kept under wet and dry conditions on the time of loading.

TABLE I Meyer number, n, maximum hardness, H_{max}, constant hardness, H_{const}, and dislocation density, ϱ, for lead sulphide samples subjected to different heat treatments

Specimen	n	H_{max} (kg mm^{-2})	H_{const} (kg mm^{-2})	ϱ (cm^{-2})
Heated at 210° C, air quenched	2.404	97	85	3×10^7
Heated at 370° C, air quenched	2.424	90	83.5	3×10^7
Heated at 480° C, air quenched	2.506	74	74	8×10^6
Heated at 570° C, air quenched	2.495	80.5	76	1.6×10^7
Annealed at 750° C, slowly cooled	2.506	74	74	$3–5 \times 10^6$
Heated at 750° C, quenched in water	2.495	80.5	76	2×10^7

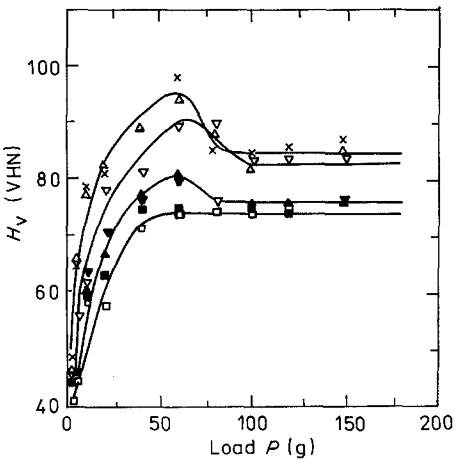

Figure 3 Plots of the load dependence of microhardness of the (1 0 0) face of PbS crystals subjected to different heat treatments. (x) Untreated; quenched from (△) 210° C, (▽) 370° C, (□) 480° C, (▲) 570° C, (▼) 750° C; (■) annealed at 750° C.

The dependence of the stress parameter P/l^2 on load, as illustrated in Fig. 4, is similar to the dependence of microhardness on load shown in Fig. 3.

The data on the dependence of microhardness on indentation load for untreated samples kept in dry and wet conditions, as well as for untreated freshly cleaved samples, are presented in Fig. 5. It may be seen that the microhardness of the samples under dry conditions closely follows the values obtained on freshly cleaved samples. Furthermore, the "dry" sample exhibits a definite maximum which is absent in the case of the "wet" sample. It may be noted that the behaviour of the hardness–load curves for crystals having low dislocation densities and for those subjected to wet conditions is similar.

4. Discussion

In order to explain the dependence of microhardness on load in a complex manner, it is first necessary to establish that it is not due to errors involved in impression measurements and load determination. The former types of error are usually observed at low loads and the peak originating therefrom also occurs at low values (e.g. 10 to 20 g) of loads. The fact that the length, l, of the rosette reduces, to a large extent, the errors in the measurement of the indentor impression even at low loads, and that the maxima in the curves of the dependence of H_v and P/l^2 on load, P, are observed at the same load of 60 g, indicates that the errors in measuring the impression diagonal are negligible. Moreover, the plots of d^2 against P for a few sets of measurements showed that the curves do pass through the origin, suggesting practically zero loading error. Therefore it may be concluded that the curves of the dependence of H_v on P are typical for the investigated specimens.

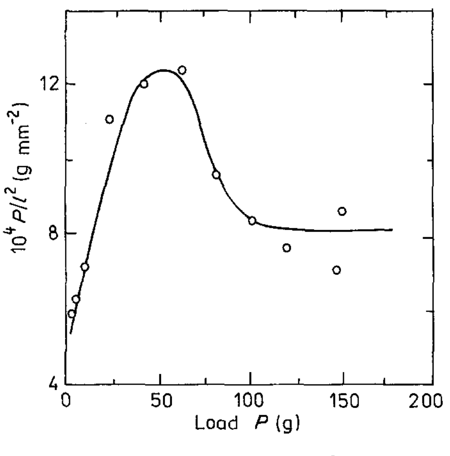

Figure 4 Dependence of stress parameter, P/l^2, on the applied load, P, for the (1 0 0) face of an untreated PbS crystal.

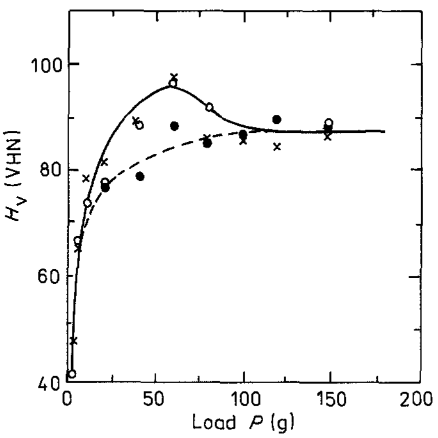

Figure 5 Curves of the load dependence of microhardness of the (1 0 0) face of thermally untreated PbS crystals kept in (○) dry and (●) wet conditions and (x) for a freshly cleaved sample.

In the case of the load-independent microhardness, i.e. $H_v = 1.854P/d^n$, the Meyer number $n = 2$. However, when H_v regularly decreases or increases with an increase in P, $n < 2$ or $n > 2$, respectively. Our plots of log P against log d, illustrated in Fig. 6 for some samples, show that each curve has two different slopes. For loads below and above about 60 g, $n > 2$ and $n = 2$, respectively. The calculated values of n for $n > 2$ are included in Table I.

First we consider the effect of the possible incorporation of air components into the crystals on their hardening. Seltzer [21] observed that the hardness of n-type PbS crystals is independent of free electron concentration, whereas that of p-type crystals increases rapidly with an increase in the hole concentration. The main components of the air that can affect the hardness of the crystals by diffusing into them are oxygen and nitrogen. As both of these are acceptor impurities, their introduction into the crystals should lead to an increase in hardness. A steady decrease in hardness with a decrease in dislocation content suggests, however, that the incorporation of the air constituents into the PbS crystals is negligible during their heating.

It may be noted from Table I that H_{max}, H_{const} and n, all the three, depend on the dislocation density, ϱ. The dependences illustrated in Figs 7 and 8 show that the hardening of the crystals, as represented by an increase in H_{const} and by a decrease in n, is a linear function of ϱ. Moreover, the values of H_{max} also increase linearly with ϱ.

The load-independent hardness H_{const}, which is proportional to dislocation density, ϱ, suggests that the hardness increase is due to the interaction of mobile dislocations with the dislocation network present in the

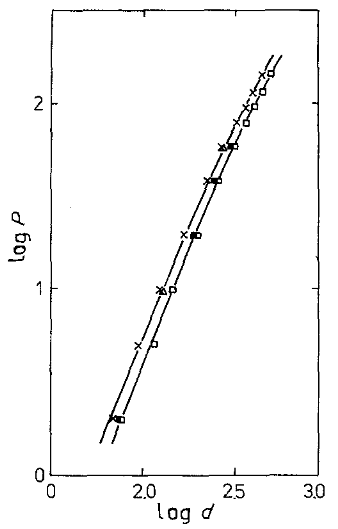

Figure 6 Plots of log P against log d for the (1 0 0) face of PbS crystals subjected to different thermal treatments. (x) Untreated; quenched from (△) 210° C, (□) 480° C; (■) annealed at 750° C.

crystal [22]. However, to explain the load- and time-dependences of hardness and connection between H_{max} and dislocation density, we consider the existence of a distorted zone near the crystal–medium interface and the effect of adsorption of water on this zone.

It is often found that the hardness of crystals decreases with an increase in the duration of indentation. This decrease in hardness has been attributed to either vibrational effects [1, 2] or OH^- adsorption [8, 9]. The results of the present work (Figs 2 and 5) suggest the latter hypothesis that the adsorption of water molecules affects hardness. The slow decrease in hardness with an increase in time (Fig. 2) and the reduction of the maximum hardness under wet conditions (Fig. 5) may be explained in terms of the time required for water (i.e. OH^-) to reach and lubricate the newly created surface along the indentor–specimen interface developed during the indentation process. This mechanism operates through the adsorption of water at the surface, which leads to the relaxation of the local changes in the lattice. This type of surface perturbation is expected to be pronounced in covalent and ionic solids because of the presence of unsatisfied bonds on their surfaces. Moreover, the surface perturbations caused by adsorption may be considered to affect the crystal lattice up to a finite depth resulting in a distorted zone at the crystal–medium interface.

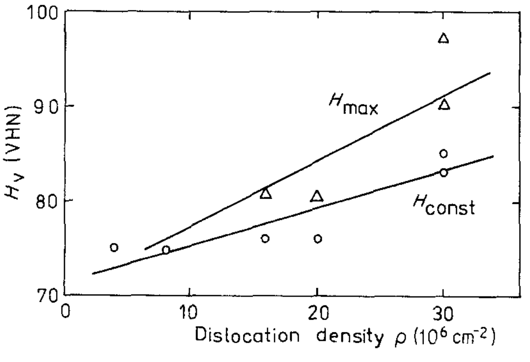

Figure 7 Curves of the dependence of H_{max} and H_{const} on dislocation density, ϱ, of PbS crystals.

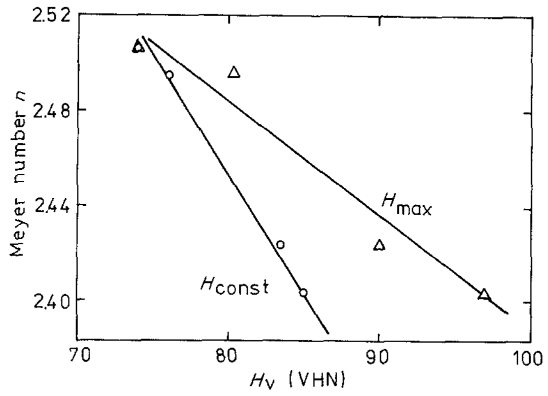

Figure 8 Relationship between Meyer number, n, and microhardness, H_{max} and H_{const}.

The variation in microhardness with load may be interpreted in terms of the effect of the distorted zone adjoining the crystal–medium interface on hardness, as explained by Berzina *et al.* [4]. During indentation, the indentor penetrates to a depth comparable with, or greater than, the thickness of the distorted zone. At comparatively low loads when the effect of this zone is marked, there is a steady increase in microhardness with load. As the depth of the indentor increases with load, the effect of the distorted zone decreases and hence the load dependence of hardness is less. For large loads when the indentor penetrates a depth at which undistorted material exists, the microhardness is independent of load.

The maxima in the hardness against load curves may be attributed to self-induced surface effects in which adsorption of water at the surface relaxes the local changes in the lattice [8, 9]. The different values of the maximum for different samples are attributed to the influence of dislocations on the adsorption of water. The results indicate that the higher the dislocation content in a crystal, the higher the value of H_{max} and the lower the adsorption of water on the surface. This means that better adsorption takes place on a perfect crystal lattice.

The question of determining microhardness of materials, independent of the influence of load, has also been discussed in recent years [23–26]. In these papers two approaches have been followed. According to the first approach [23, 24], the dependence of microhardness on load at low loads is due to the contribution of the surface energy of the solid but it is constant in the bulk of the material. In principle this approach is similar to that followed in the present paper. It has also been suggested [23] that cracks developed at the corners and the sides of an indentation impression can equally lead to a divergence in microhardness at low loads. According to Weiss [26], the contribution of surface energy and cracks in causing the divergence at low loads is extremely small. He advances an alternative approach in which he mainly considers elastic displacement from the recorded impression and errors in the measurement of the indentation impression.

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