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Hardness anisotropy of SrF_2, BaF_2, NaCl and AgCl crystals

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The value of Knoop microhardness was obtained for crystals of SrF_2, BaF_2, NaCl and AgCl by indentation in various directions on several crystallographic planes. In all cases, the hardness is essentially dependent on the crystallographic direction along the long axis of the indentor and independent of the plane of indentation, as first reported by Garfinkle and Garlick for other cubic crystals. In addition, although the absolute value of hardness varies from one crystal to another, the hardness anisotropy was quite similar for all crystals. Since the primary slip mode is different among the crystals tested, it is concluded that hardness anisotropy cannot be used to determine the primary slip mode.

1. Introduction

The hardness test has been used for a long time as a simple means of characterizing the mechanical behaviour of metals and minerals. In particular, the Knoop hardness test has proved valuable in the study of plastic anisotropy in single crystals. The geometry of the Knoop indentor is such that the size of the indentation is sensitive to crystal orientation. The early work of Daniels and Dunn [1] has paved the way for an explanation of hardness anisotropy based on the Schmid Law for slip. Several extensions and alternative models have been added since then [2-4].

Experimentally, Garfinkle and Garlick [5] have found that for several cubic crystals, the Knoop hardness number (Khn) is essentially dependent on the crystal direction along the long axis of the indentor and not on the plane of indentation. Brookes *et al* [3] noted that this orientation dependence is related to the primary slip mode of the crystal. Magnesium oxide and lithium fluoride, for example, exhibit a {110} ⟨110⟩ primary slip mode and also an increasing hardness value from ⟨100⟩ to ⟨110⟩ to ⟨111⟩. Calcium fluoride, on the other hand, exhibits a {100} ⟨110⟩ primary slip mode and a decreasing hardness value for the above sequence of orientations. They suggested that hardness anisotropy might be used to identify active slip systems. This suggestion was taken up by Hannink *et al* [6] in studying transition-metal carbides. The latter are normally brittle at room temperature and hence their slip behaviour cannot be ascertained readily. The use of hardness anisotropy for identification of active slip systems is limited, however, in that two (or more) slip modes may give rise to the same anisotropy. Hannink *et al*, for example, clearly recognized that both {111} ⟨110⟩ and {100} ⟨110⟩ slip modes appear to give the same anisotropy, at least for indentation on the {100} plane.

In this study, we investigated the Knoop hardness anisotropy of several cubic crystals with known differences in their primary slip modes. Strontium fluoride and barium fluoride, like calcium fluoride, exhibit a {100} ⟨110⟩ primary slip mode. Sodium chloride exhibits a {110} ⟨110⟩ primary slip mode, and silver chloride slips primarily by ⟨110⟩ pencil glide. Sufficient crystal directions on several crystal planes were indented to check the validity of the Garfinkle and Garlick results for these crystals and also to compare the data among crystals over a large range of orientations.

2. Experimental

The strontium and barium fluoride single crystals were grown at Optovac by the Stockbarger-Bridgman method. The powdered com-

pound was melted in a conical-tipped graphite crucible and then directionally solidified by slowly lowering the melt in the furnace. The process was carried out under high vacuum, and a small amount of lead fluoride (~ 2 wt %) was added to reverse any hydrolysis reaction that might have previously occurred and to prevent further reaction with water vapour during growth. The lead is absent in the as-grown crystal as per spectroscopic analysis.

Specimens with four planes, {100}, {110}, {111} and {112}, were oriented by X-rays and cut on a diamond wheel. They were then polished mechanically on Texmet (Buehler) paper with 12 μm Al_2O_3, 6 and 1 μm diamond paste successively. X-ray Laue spots remained sharp after this procedure.

The sodium chloride and silver chloride crystals were supplied by Harshaw Chemical Company in the polished condition. There were two samples of AgCl, one with a {100} and one with a {110} surface. One NaCl crystal had a polished {110} surface, and another was cleaved on a {100} surface for indentation.

Microhardness tests were conducted on a Kentron tester using a Knoop diamond indentor. A load of 300 g weight was used for SrF_2 and BaF_2, and 25 g weight was used for NaCl and AgCl. The average value of five readings for each orientation was computed. Scatter in the data is generally within ± 5%.

3. Results

3.1. SrF_2 and BaF_2

Fig. 1 shows the variation of Khn with the direction of the long axis of the indentor for the four crystal planes. From these data the values of Khn for a large number of indentation directions common to two or more indentation planes were extracted. Table I lists such values for SrF_2 and BaF_2. It can be seen that the value of Khn is essentially dependent on the direction of indentation and independent of the plane of indentation, as Garfinkle and Garlick have found for other cubic crystals.

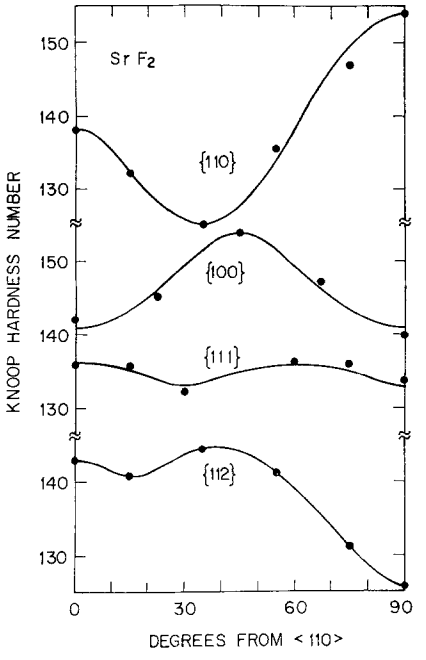

Figure 1 Variation of Khn with direction for indentation on four planes. Data for SrF_2.

In Fig. 2 we plotted contours of constant Khn

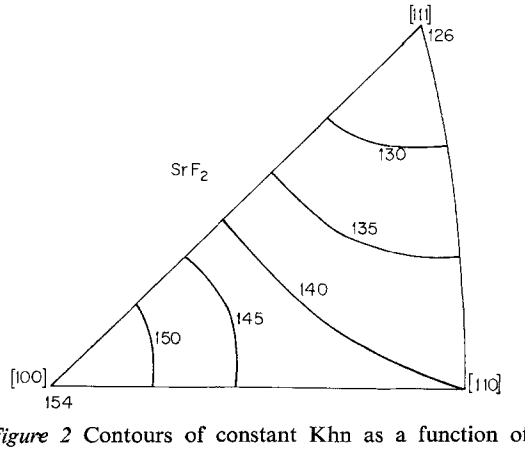

Figure 2 Contours of constant Khn as a function of indentation direction represented by standard stereographic triangle. Data for SrF_2.

TABLE I Knoop hardness data for SrF_2 and BaF_2

Direction	Plane	SrF_2	BaF_2
⟨100⟩	{110}	154	89
	{100}	154	85
⟨110⟩	{110}	138	76
	{100}	141	78
	{111}	136	75
	{112}	143	76
⟨111⟩	{110}	125	70
	{112}	126	72
⟨112⟩	{110}	136	77
	{111}	133	74
⟨210⟩	{100}	144	80
	{112}	142	76
⟨321⟩	{111}	135	75
	{112}	135	75

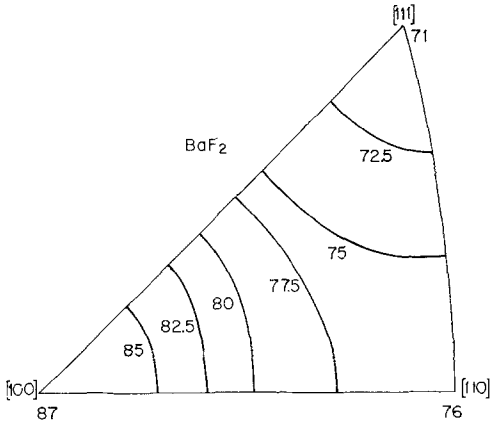

Figure 3 Same as Fig. 2, data for BaF_2.

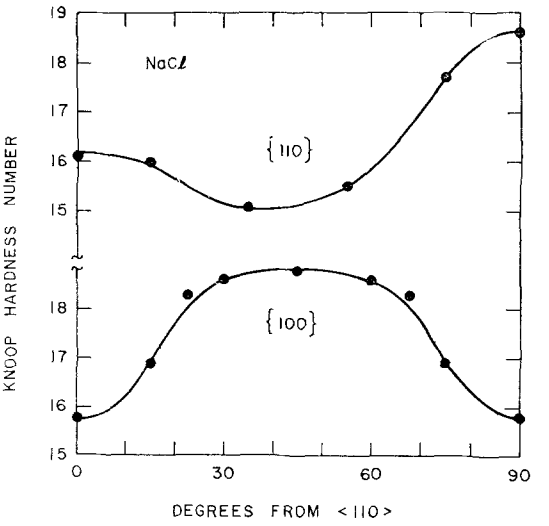

Figure 4 Variation of Khn with direction for indentation on {110} and {100} planes of NaCl.

for SrF_2 as a function of indentation direction as represented within the standard stereographic triangle. A similar plot for BaF_2 is presented in Fig. 3. The variation of Khn with orientation is similar for both crystals, the hardest direction being ⟨100⟩ and generally decreasing towards ⟨110⟩ and then ⟨111⟩. The ratio of Khn for ⟨100⟩:⟨110⟩:⟨111⟩ is also very close for the two crystals. Previously Ballard *et al* [7] reported a value of Khn = 82 for BaF_2 using a 500 g weight load, but did not mention the indentation direction. This value falls within those shown in Fig. 3. The authors are not aware of previously reported values of Khn for SrF_2.

3.2. NaCl

Fig. 4 shows the variation of Khn with indentation direction on {110} and {100} planes of NaCl. These variations are similar to those for SrF_2 and BaF_2. Although these two planes provide data only for directions on the boundaries of the stereographic triangle and not inside it, we took the liberty of drawing the contours in Fig. 5 on the expectation that the hardness varies with orientation in a smooth fashion. Again the hardness decreases in the order of ⟨100⟩:⟨110⟩:⟨111⟩. Previously, values have been reported for ⟨100⟩ and ⟨110⟩ [3, 8, 9]. These compare quite well with the exception of the ⟨110⟩ value quoted by Brookes *et al* [3]. Their ⟨110⟩ value was greater than that for ⟨100⟩, whereas the opposite was reported in the other works.

3.3. AgCl

Hardness plots for {110} and {100} planes were obtained for AgCl. They are similar to those for NaCl. An estimated contour plot is shown in Fig. 6. Previously Combes *et al* [8] reported a value of Khn = 9.5 for AgCl, considerably higher than the present values. While the source of the discrepancy is unknown, it is speculated that the value reported by Combes *et al* was for a rolled polycrystalline slab of AgCl.

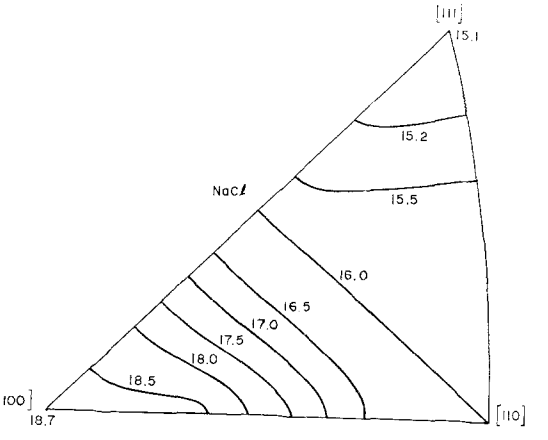

Figure 5 Orientation dependence of Khn for NaCl.

4. Discussion

The striking observation regarding the present results is that despite the differences in primary slip mode among the various crystals tested, the hardness anisotropy is remarkably similar. This similarity is further brought out by the compilation in Table II of the hardness of several major orientations. Included in Table II are data for

TABLE II Knoop hardness number in several major crystallographic directions for several cubic crystals. (Values inside parentheses are normalized with respect to ⟨100⟩.)

Crystal	Slip mode	⟨100⟩	⟨210⟩	⟨110⟩	⟨211⟩	⟨111⟩
CaF_2*	{100}⟨110⟩	178 (1.0)	—	160 (0.90)	158 (0.89)	—
SrF_2	{100}⟨110⟩	154 (1.0)	143 (0.93)	140 (0.91)	135 (0.87)	126 (0.81)
BaF_2	{100}⟨110⟩	87 (1.0)	78 (0.90)	76 (0.87)	76 (0.87)	71 (0.82)
Al†	{111}⟨110⟩	22.6 (1.0)	19.9 (0.88)	17.8 (0.79)	18.3 (0.81)	16.9 (0.75)
NaCl	{110}⟨110⟩	18.7 (1.0)	17.5 (0.94)	16.0 (0.86)	15.5 (0.83)	15.1 (0.81)
AgCl	⟨110⟩ pencil glide	6.3 (1.0)	5.4 (0.86)	5.1 (0.81)	5.0 (0.79)	5.0 (0.79)

*Brookes *et al* [3]; †Garfinkle and Garlick [5].

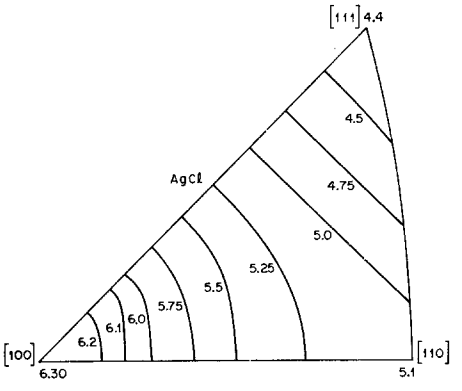

Figure 6 Orientation dependence of Khn for AgCl.

CaF_2 from Brookes *et al* [3] and for Al from Garfinkle and Garlick [5]. It may be seen that except for ⟨110⟩ versus ⟨211⟩ for Al, the hardness values decrease in the sequence ⟨100⟩: ⟨210⟩:⟨110⟩:⟨211⟩:⟨111⟩ for all crystals, with some toss-up between ⟨110⟩ and ⟨211⟩. Even the ratio of $H_{\langle 100\rangle}/H_{\langle hkl\rangle}$ is reasonably similar among the various crystals. Hence different primary slip modes can give rise to essentially the same hardness anisotropy. Conversely, crystals with the same primary slip mode have been known to exhibit a different hardness anisotropy. According to the tabulation of Brookes *et al* [3], the primary slip mode of MnS, LiF, MgO, and MnO is {110} ⟨110⟩, and yet for all these crystals the hardness generally increases in the sequence ⟨100⟩:⟨110⟩:⟨111⟩, opposite to that for NaCl. NaBr, KCl, KBr, and KI behave similarly to NaCl [9]. It must thus be concluded that hardness anisotropy is an unreliable indicator of primary slip modes.

One main consideration in attempting to relate the hardness to a primary slip mode is the necessity for activating five independent slip systems in the absence of cracking, since an arbitrary shape change requires five independent slip systems [10]. Some of the slip modes, for example {100} ⟨110⟩ and {110} ⟨110⟩, do not possess five independent slip systems. Hence the activation of secondary slip systems is required. The hardness value would then have to be assessed based on the activation of perhaps two or more slip modes and the differences in stresses required to activate these modes. This aspect is under current investigation.

5. Summary

The Knoop hardness was determined for SrF_2, BaF_2, NaCl and AgCl by indentation on several crystallographic planes and with the long axis of the indentor aligned in various crystallographic directions. The following results were obtained.

1. The value of Khn is essentially dependent on the indentation direction and independent of the plane of indentation, in agreement with the observation of Garfinkle and Garlick on other cubic crystals.
2. Despite differences in primary slip mode among the crystals tested, the hardness anisotropy is remarkably similar. The hardness essentially decreases in the sequence of ⟨100⟩ → ⟨110⟩ → ⟨111⟩ directions.

Acknowledgements

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