JOURNAL OF MATERIALS SCIENCE 19 (1984) 2582–2592

Microhardness measurements on single crystals of flux-grown rare earth perovskites (orthoferrites, orthochromites and aluminates)

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The results of indentation-induced microhardness testing studies of flux-grown single crystals of rare earth orthoferrites, $RFeO_3$ (R = Gd to Er and Yb), rare earth orthochromites $RCrO_3$ (R = La, Eu and Dy), and rare earth aluminates $RAlO_3$ (R = La, Sm, Gd, Eu and Ho) are presented. The variation in the value of microhardness with load is observed to be non-linear in the case of all these materials. It is found that the results are not in accordance with Kick's law. The results have been analysed and the applicability of the idea of materials resistance pressure in the modified law as proposed by Hays and Kendall [*Metallography* **6** (1973) 275] is discussed.

1. Introduction

The rare earth orthoferrites, orthochromites and aluminates have in common a structure which is only slightly distorted from the perfect cubic perovskite. These materials are of considerable interest on account of their magnetic and optical properties [1–3]. It may, however, be mentioned that practically no work has so far been reported on the mechanical properties of these materials.

Three methods are commonly used for studying the mechanical properties of crystals. They are: (a) measurements of the microhardness, using microhardness tester on a PMT-3 apparatus (manufactured by Vickers UK) or mhp 100 (manufactured by Carl Zeiss, Germany); (b) compression tests on an apparatus for microchemical material testing [4]; and (c) studies of the star dislocations which are formed by a diamond indentor. In order to understand the mechanical behaviour of materials, much work has been carried out on different materials [5–15]. To the best of author's knowledge, no important data concerning the mechanical properties of rare earth perovskites (orthoferrites, orthochromites and aluminates) have been reported. Having undertaken investigations on the mechanical properties of these materials, the authors present, in this paper, the results of indentation-induced hardness testing studies on rare earth orthoferrite crystals $RFeO_3$ (R = Gd to Er and Yb), rare earth orthochromites $RCrO_3$ (R = La, Eu and Dy) and rare earth aluminates $RAlO_3$ (R = La, Sm, Eu, Gd and Ho).

2. Experimental procedure

The crystals of rare earth perovskites used in the present investigation were prepared by the flux technique [16]. Samples approximately 4 mm × 2 mm × 1.5 mm were used for microhardness studies. The measurements were carried out at room temperature (30° C) using a Vickers microhardness tester mhp 100 attached on an incident light metallurgical research microscope Neophot-2 made by Carl Zeiss, Germany. Crystal samples with plane surfaces were selected and then mounted and cemented. Different loads ranging from 20 to 100 g were used for indentation while keeping the time of indentation at 2 sec. For hardness determination, the crystals were indented at different

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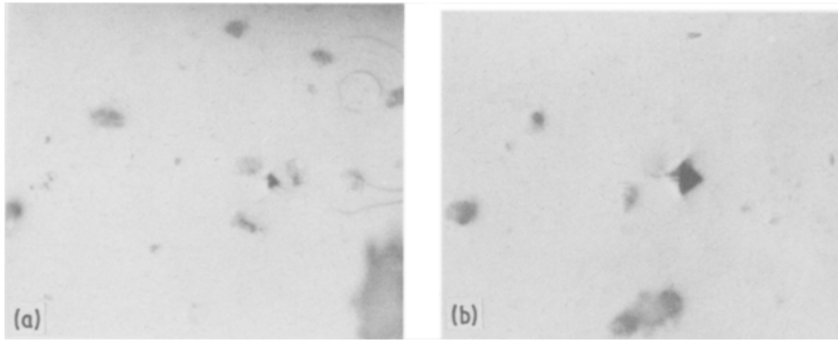


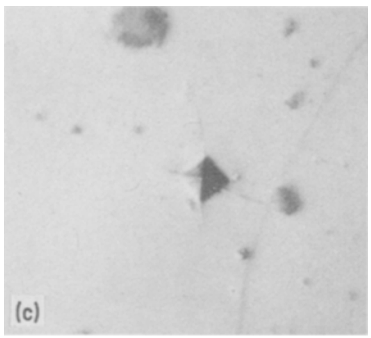


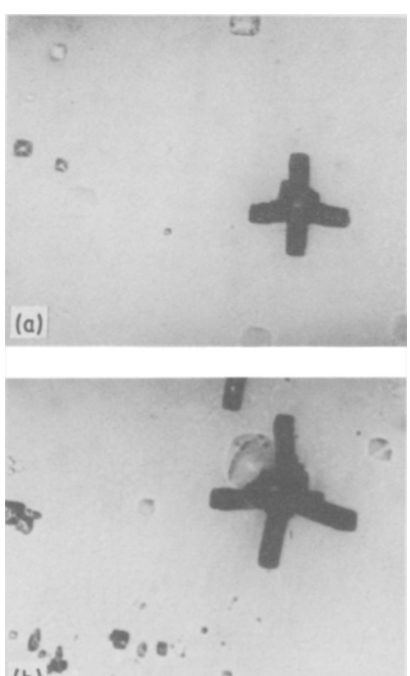
Figure 1 Indentor impressions at various loads on the $LaAlO_3$ crystal surface. Indentor loads (a) 20 g, (b) 65 g, (c) 100 g, respectively (X 500).

sites so that the distance between the two indentations was more than 3 times the diagonal length. This was done to ensure surface effects were independent of one another. The indented impressions were approximately square. The diameter of the indentor mark was measured with the help of a filar eye-piece with a minimum count of 0.25 μm (x 500). The value of microhardness was calculated using the expression $H = 1.8544 \times P/d^2$ kg mm^{-2} where P is the applied load in g and d is the diagonal length of the indentor impression in μm. The microhardness of a particular sample was calculated by averaging the different values of microhardness at different loads.

For etching experiments, a $LaAlO_3$ crystal was placed in 20% HNO_3. The test tube containing HNO_3 was placed in a water bath maintained at a constant temperature of 95° C.

3. Results

It is difficult to obtain cleaved surfaces of rare earth perovskites, and so plane surfaces, microscopically free from signs of any damage, were chosen for the indentation purposes. Fig. 1 shows the impression of indentations made on $LaAlO_3$ crystal at different loads, 20, 65 and 100 g respectively. It is clearly observed from the representative photographs of Fig. 1 that the size of the impression increases with the load. Figs. 2a, b and c show



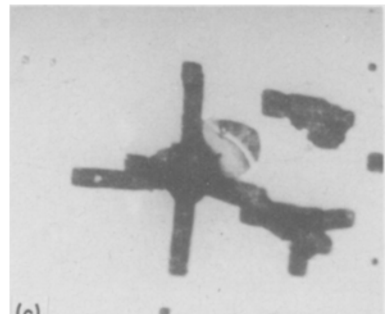


Figure 2 Corresponding rosette pattern of Fig. 1 after 3 h of etching (X 500).

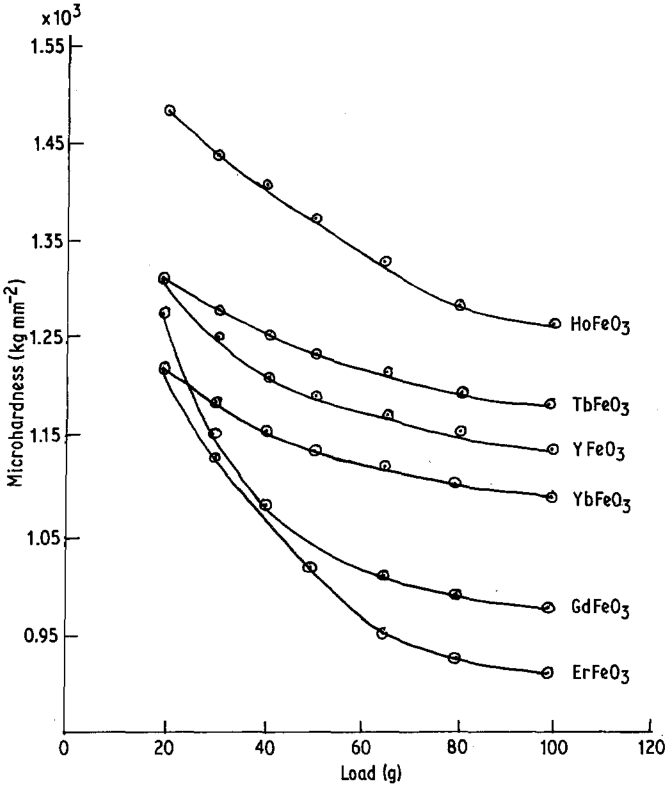


Figure 3 Variation of microhardness with applied load in the case of rare earth orthoferrites.

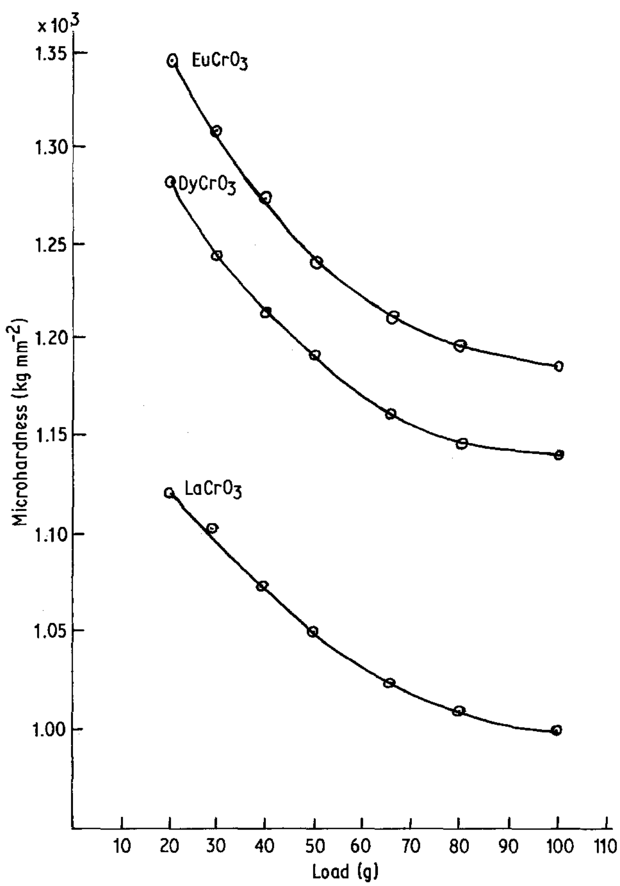


Figure 4 Variation of microhardness with applied load in the case of rare earth orthochromites.

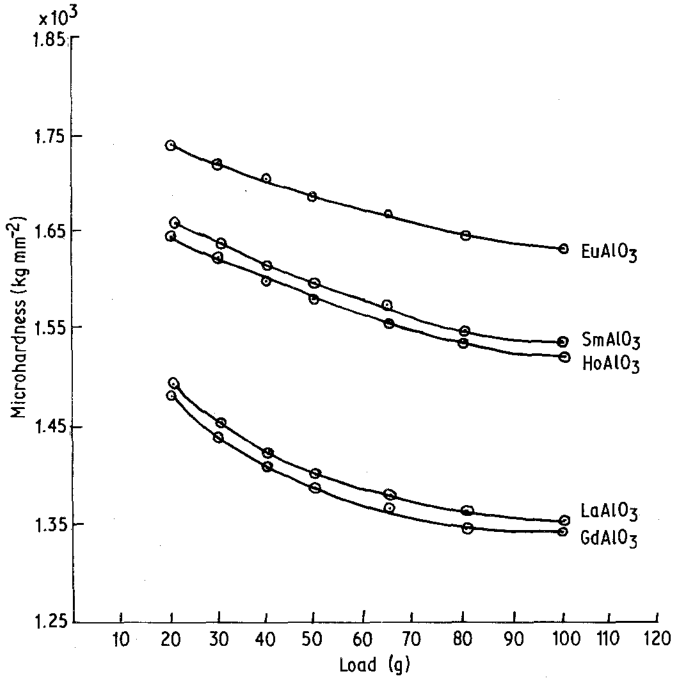


Figure 5 Variation of microhardness with applied load in the case of rare earth aluminates.

the corresponding "rosette" pattern around the microhardness indentation mark of Figs. 1a to c after etching in 20% HNO_3 for 3 h. These figures show clearly that the length of the "rosette" arm increases with load. It has been reported earlier that the size of the dislocation "rosette" produced around a microhardness indentation is a useful and convenient test for the determination of mechanical strength of single crystals [17]. It has been established [18] that HNO_3 is a dislocation etchant for $LaAlO_3$ crystals. The arm lengths of the dislocation "rosette" (Fig. 2), which correspond to the distance travelled by the dislocation, decrease as the hardness increases (i.e. as the load decreases). This is attributed to the fact that the mobility of the dislocation lines increases with the load. It is because of this that microhardness decreases with increase in load. A further etching for 1.5 h in 20% HNO_3 of the same surface as Fig. 2 maintains the "rosette" pattern. The thickening of the pattern as observed on successive etching is because of repeated preferential etching along the strain pattern due to the indentation.

As stated above, the microhardness varies with load in the case of the rare earth orthoferrites, orthochromites and aluminates studied in the present investigation. Figs. 3, 4 and 5 show the variation of microhardness against load for $RFeO_3$ (R = Gd to Er and Yb), $RCrO_3$ (R = La, Eu and Dy) and $RAlO_3$ (R = La, Sm, Eu, Gd and Ho), respectively. From Fig. 3 one can see that there is a variation in the value of microhardness as load varies, though the variation is different for different materials for the same intervals of load; the value of microhardness decreases as the load increases in the case of all the materials. It is significant to note that there is a rapid fall in the value of microhardness until a load of about 65 g is reached, and thereafter there is a tendency to attain saturation. In this respect, all the curves belonging to the rare earth orthoferrites show a striking similarity, particularly between loads of 70 and 100 g. That the variation in the value of microhardness with load is non-linear in the case of all the materials is very significant in the light of the discussion that follows.

Fig. 4 shows the variation of microhardness with load in the case of rare earth orthochromites, which resembles that outlined above for rare earth orthoferrites. There is, however, more similarity in the shapes of the curves belonging to different rare earth orthochromites, on account of a similar variation of microhardness value with fixed load intervals.

The nature of the curves of Fig. 5 pertaining to rare earth aluminates differs from those of rare earth orthoferrites (Fig. 3) and orthochromites (Fig. 4) only with regard to the decrease in the microhardness value with load. The fall in the value of microhardness with load is not as rapid as in the case of Figs. 3 and 4.

TABLE I

Sample	Vickers Hardness Numbers (VHN) (kg mm^{-2})
Orthoferrites	
1. $GdFeO_3$	1081
2. $TbFeO_3$	1241
3. $DyFeO_3$	1207
4. $HoFeO_3$	1369
5. $ErFeO_3$	1036
6. $YbFeO_3$	1150
Orthochromites	
7. $LaCrO_3$	1055
8. $EuCrO_3$	1250
9. $DyCrO_3$	1197
Aluminates	
10. $LaAlO_3$	1410
11. $SmAlO_3$	1591
12. $EuAlO_3$	1682
13. $GdAlO_3$	1397
14. $HoAlO_3$	1549

From the data collected on measurements of microhardness at different loads, the microhardness values in kg mm^{-2} were computed by taking the average values, and are recorded in Table I. For assessment of the hardness of these materials, the data may be compared with the known values for a few alkali halide crystals [6, 19, 20], which range from around 9 to 20 kg mm^{-2}, whereas for the materials studied here the value ranges from 1055 to 1682 kg mm^{-2}.

4. Discussion

The results obtained from Figs. 3, 4 and 5 show that as the applied load decreases the hardness of the materials increases, whether they be rare earth orthoferrites, orthochromites or aluminates. The variations are not linear for any of the materials and are not in accordance with what is suggested by Kick's law. Upet and Varchanya [21] obtained results on alkali halide crystals which they interpreted as due to the effect of the surface on the mechanical properties of the bulk material. Hays and Kendall [22] obtained similar results for a number of metals and alloys and they explained their results in ways which are not applicable to the analysis of our results.

Kick [23] proposed an analysis of results on hardness and according to him the relation between load P and indentation length is represented by

$$P = K_1 d^n \tag{1}$$

where P is the load applied in grams, d is the observed length of indentation in μm, K_1 (standard hardness) and n are constants. Kick's analysis of hardness postulates a constant value for n to be equal to 2 for all indentors and for all geometrically similar impressions. Equation 1 was further supported by Schultz and Hanemann [24] by proposing that Vickers microhardness and macrohardness values were comparable. However, Kick's law represented by Equation 1 has not received wide acceptance on account of the fact that n usually has a value less than 2, especially in the region of low load hardness. Saraf [25] obtained two different values of n for higher and lower load regions in the case of baryte crystals. Hays and Kendall [22] attempted to overcome this difficulty by assuming that a resistance of deformation could

TABLE II Result of hardness analysis

Crystal	K_1 (kg)	n	W/K_1	K_2/K_1	K_2 (× 10^{-4} kg)	W (× 10^{-3} kg)
Orthoferrites						
1. $GdFeO_3$	0.00119125	1.7132	4.0	0.445006	5.3009	4.7648
2. $TbFeO_3$	0.00119722	1.884	1.95	0.7288	8.726	2.3345
3. $DyFeO_3$	0.00116766	1.864	3.0	0.68831	8.0367	3.5028
4. $HoFeO_3$	0.00123368	1.815	2.5	0.607251	7.4910	3.084
5. $ErFeO_3$	0.00115027	1.692	4.0	0.414878	4.7719	4.60
6. $YbFeO_3$	0.00115373	1.873	3.2	0.70381	8.1196	3.6918
Orthochromites						
7. $LaCrO_3$	0.00109417	1.863	3.75	0.6821	7.4629	4.1028
8. $EuCrO_3$	0.0011853	1.859	3.5	0.6883	6.4752	4.1485
9. $DyCrO_3$	0.00116183	1.863	2.75	0.5463	7.9968	3.19495
Aluminates						
10. $LaAlO_3$	0.0013431	1.884	3.0	0.734402	9.8637	4.0293
11. $SmAlO_3$	0.0012398	1.909	3.4	0.7893	9.7863	4.0293
12. $EuAlO_3$	0.0012904	1.913	2.0	0.7997	10.3202	2.580
13. $GdAlO_3$	0.0012214	1.879	2.2	0.7243	8.847	2.687
14. $HoAlO_3$	0.00128146	1.911	2.0	0.79146	10.1418	2.5628

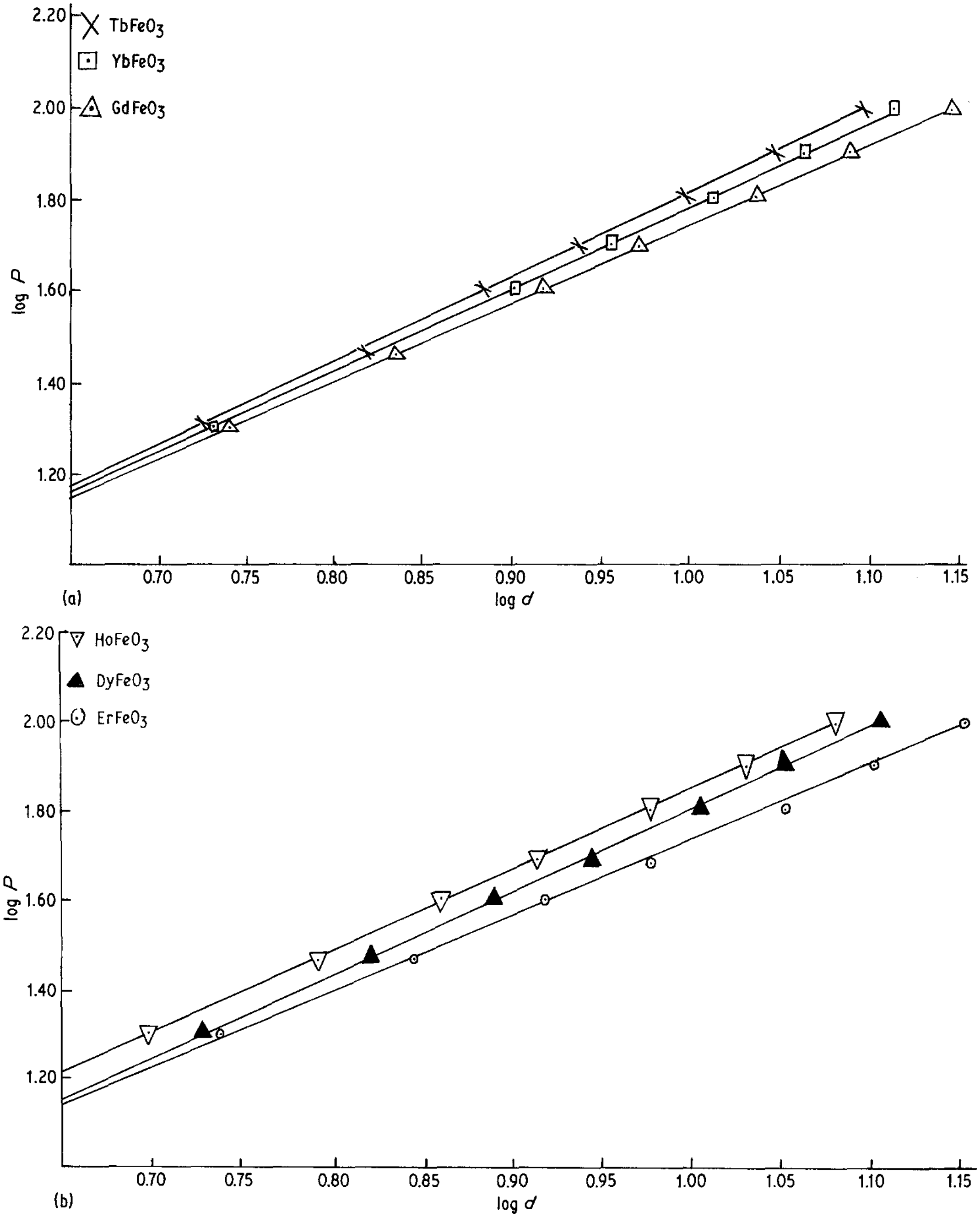


Figure 6 Variation of applied load (log P) with the Vickers diagonal (log d) for rare earth orthoferrites.

be evaluated by considering it as a Newtonian resistance pressure of the specimen itself. As load P is applied to a crystal sample, they assumed that the load P is partially affected by a smaller resistance pressure W which is a function of the material under testing. According to them, W represents the minimum applied load needed to produce an indentation, since the load W allows no plastic deformation.

Considering the sample resistance pressure W, Equation 1 is modified to:

$$P - W = K_2 d^2 \qquad (2)$$

where K_2 is constant and $n = 2$ is the logarithmic index. Since the factor W allows the limiting case to prevail where microhardness is not marked by dependence on the load, n should turn out to be equal to 2.

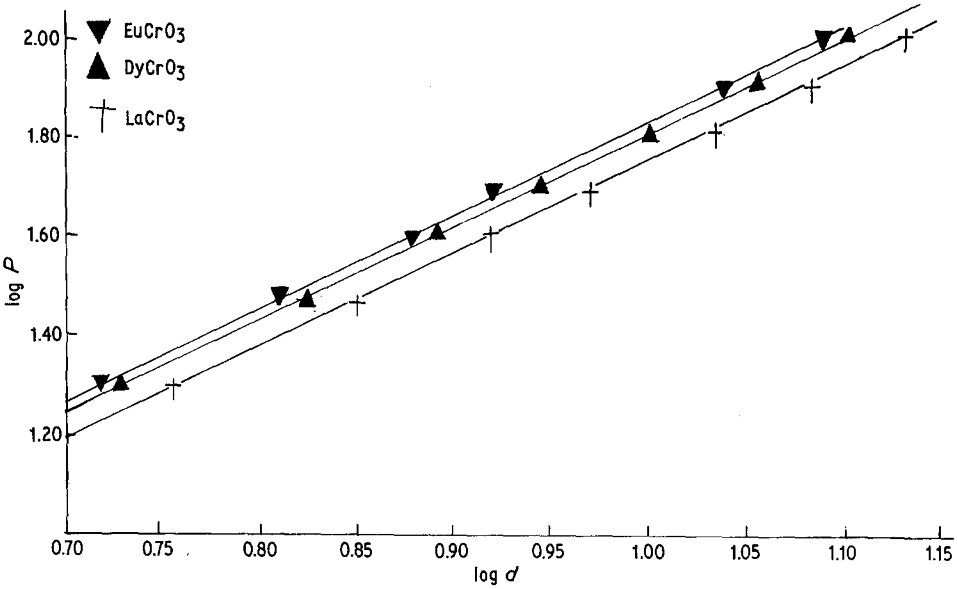


Figure 7 Variation of applied load (log P) with the Vickers diagonal (log d) for rare earth orthochromites.

Solving Equations 1 and 2 we obtain,

$$W = K_1 d^n - K_2 d^2 \quad (3)$$

From this

$$d^n = W/K_1 + K_2/K_1 d^2 \quad (4)$$

It is now possible to apply these equations by ordinary graphical methods. A logarithmic form of Equation 1 indicates that if log P is plotted against log d, we are in a position to obtain slope n and the intercept log K_1 (from which K_1 can be obtained). Figs. 6 to 8 represent the dependence of log P on log d for the data obtained on rare earth orthoferrites, orthochromites and aluminates, respectively. The values of K_1 and n as obtained from Figs. 6 to 8 are recorded in Table II for different materials as indicated. From these calculations one finds that $n < 2$.

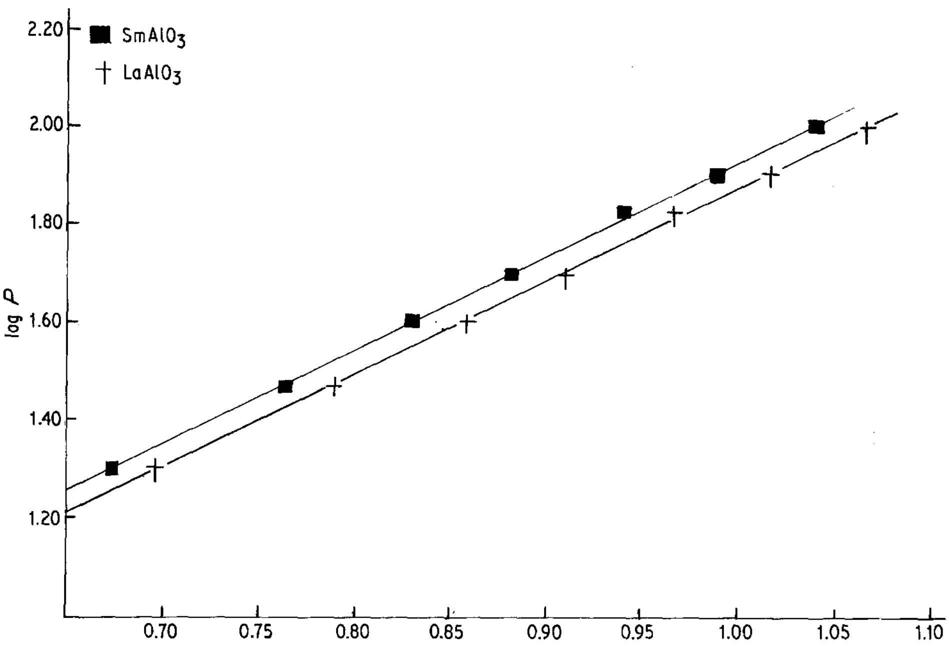


Figure 8 Variation of applied load (log P) with the Vickers diagonal (log d) for rare earth aluminates.

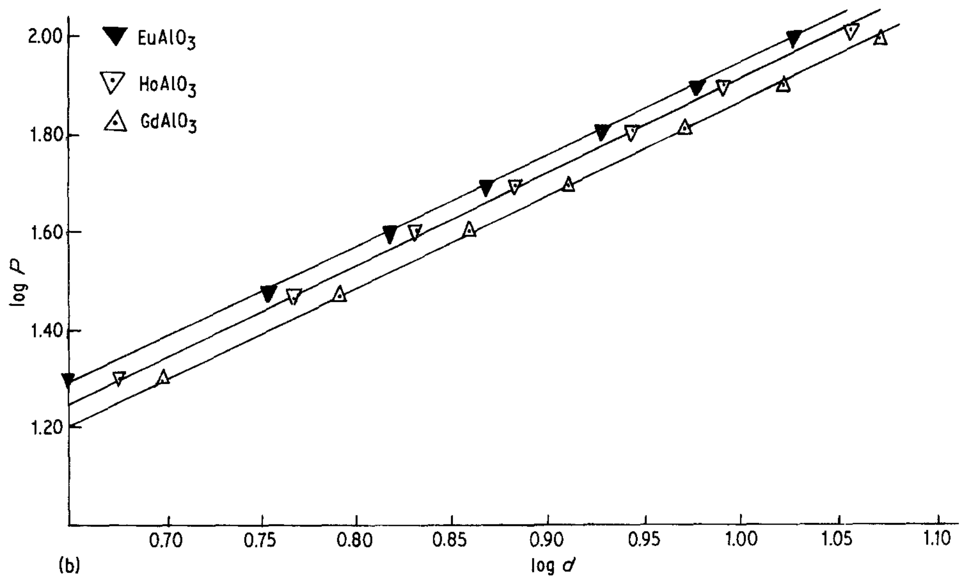


Figure 8 Continued.

A cartesian plot of Equation 4 suggests that if d^n is plotted against d^2, it should yield the slope K_2/K_1 and the intercept W/K_1. Having already determined K_1 from the logarithmic plot of P and d, one can obtain the values of K_2 and W. A graph of d^n against d^2 yields a straight line in the case of orthoferrites, orthochromites and aluminates. Fig. 9 shows a graph of d^n against d^2 for the rare earth orthochromites. Similar curves are obtained for the rest of the materials. The values of W/K_1 (intercept) and K_2/K_1 (slope) as obtained from these curves are given in Table II for the materials under investigation. The values of K_2 and W calculated by substituting the values of K_1 are also given in Table II. Table II is thus a compiled key data obtained on these materials in the application for our analysis of hardness for the rare earth orthoferrites, orthochromites and aluminates.

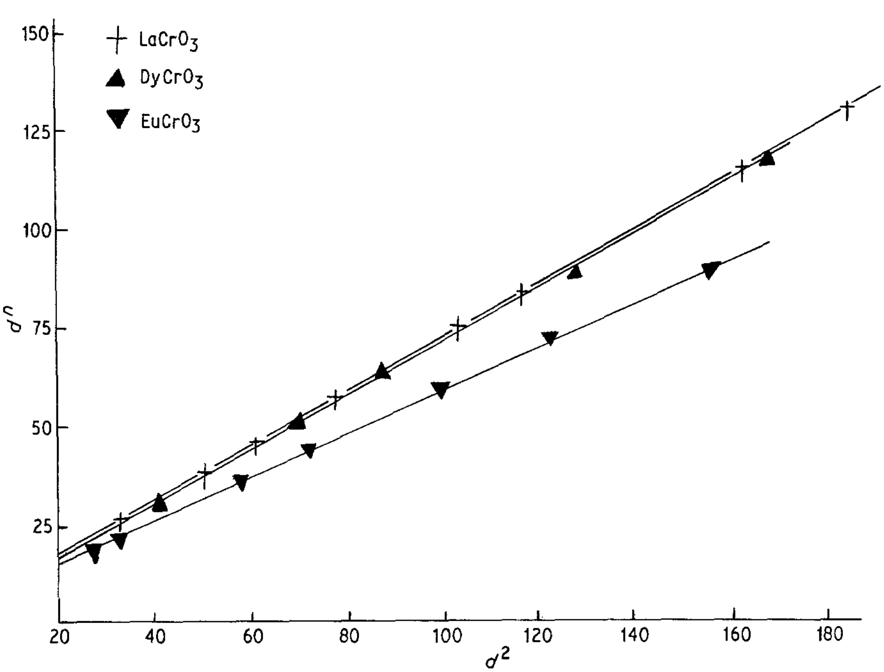


Figure 9 Graph of d^n against d^2 for rare earth orthochromites.

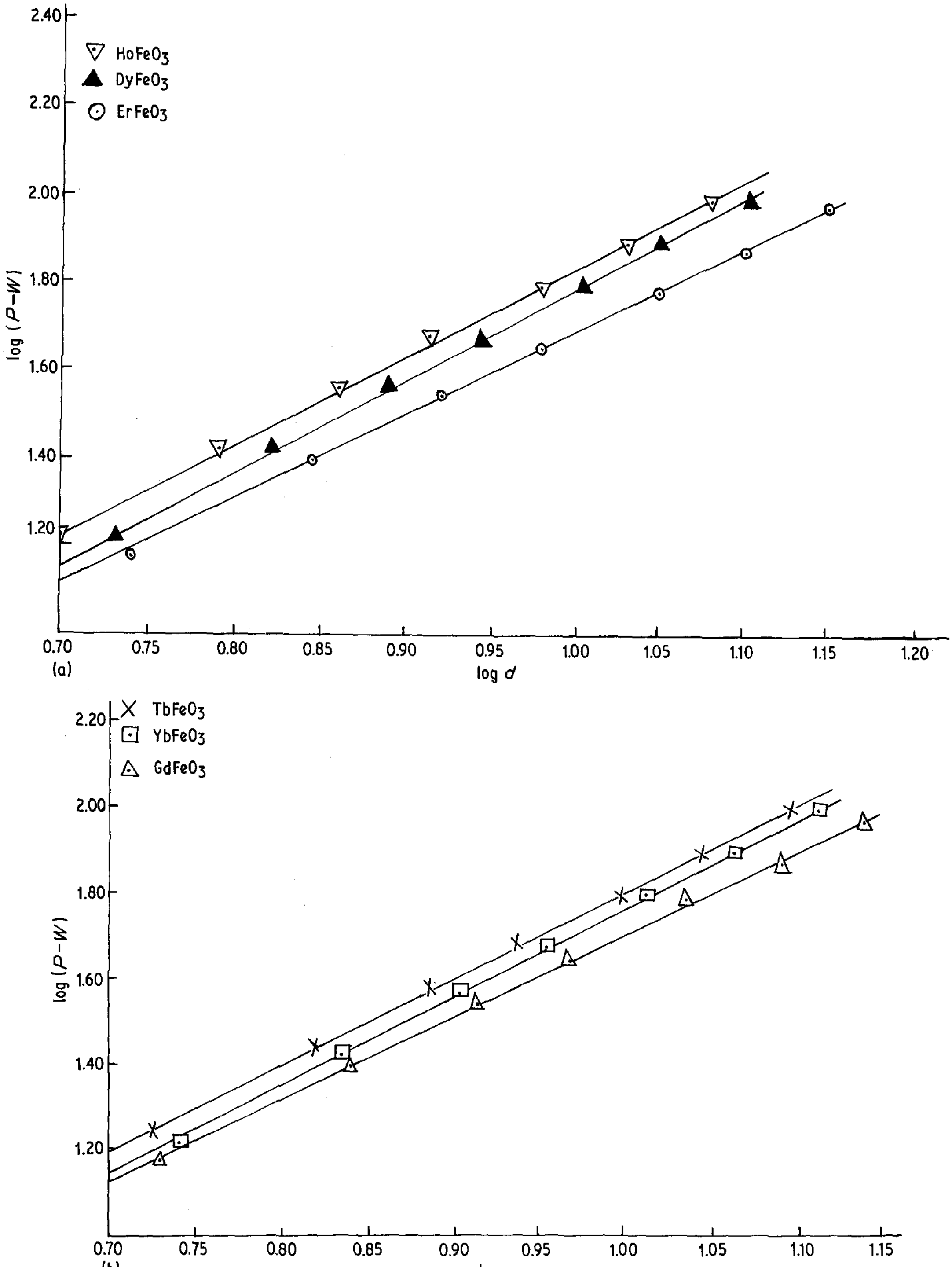


Figure 10 Relationship between true applied load log $(P - W)$ and the Vickers diagonal (log d) for rare earth orthoferrites.

Figs. 10 to 12 are the graphs in which the true applied load log $(P - W)$ is plotted against the logarithm of the Vickers diagonal, i.e. log d (from the data obtained in the case of materials under investigation). From these graphs, n is found to be equal to 2 in all cases, in accordance with the assumption of resistance pressure of the crystal specimen, as proposed by Hays and Kendall [22] and found applicable to alkali halide crystals by Pratap and Hari Babu [6]. It is thus concluded that

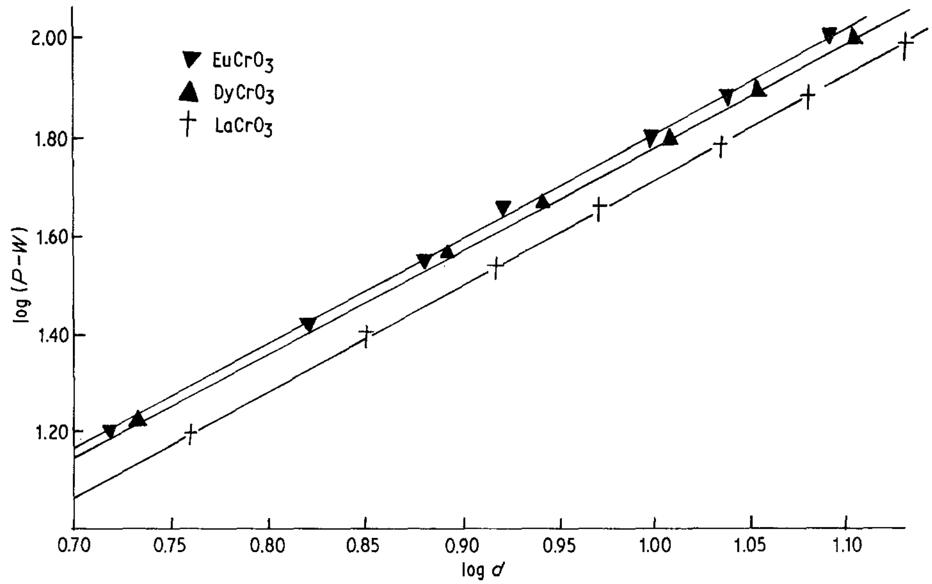


Figure 11 Relationship between true applied load log $(P-W)$ and the Vickers diagonal (log d) for rare earth orthochromites.

rare earth orthoferrites $RFeO_3$ (R = Gd to Er and Yb), orthochromites $RCrO_3$ (R = La, Eu and Dy) and aluminates $RAlO_3$ (R = La, Sm, Eu, Gd and Ho) fall in the class of materials to which the idea of resistance pressure as proposed by Hays and Kendall is applicable.

Acknowledgement

One of us (KKR) is grateful to the University authorities for the award of a University Fellowship. This work is under a collaborative research programme between the Physics department, University of Jammu and the Clarendon Labora-

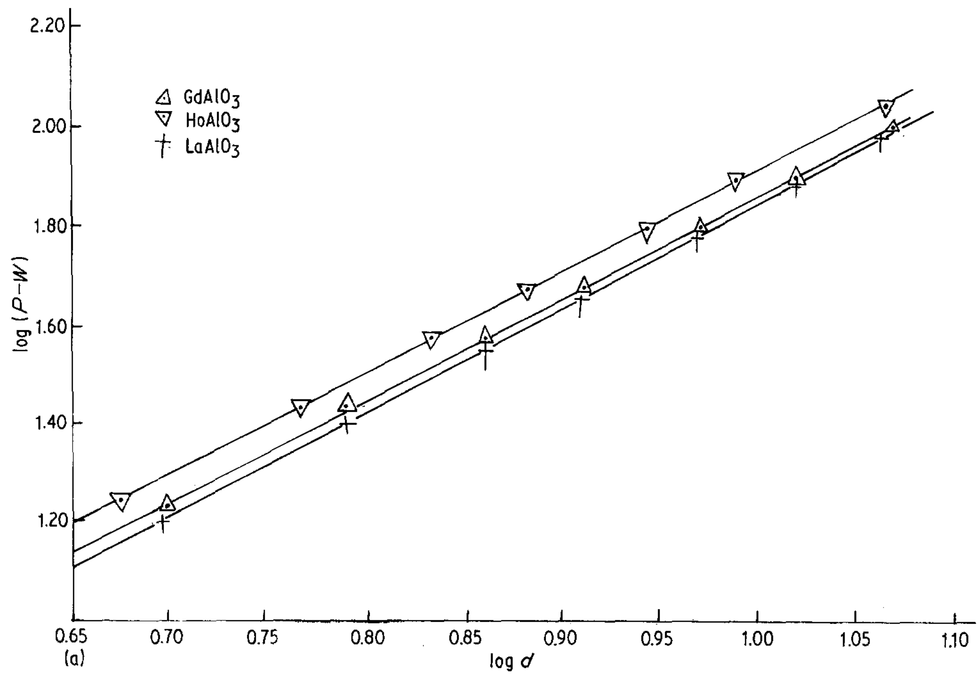


Figure 12 Relationship between true applied load log $(P-W)$ and the Vickers diagonal (log d) for rare earth aluminates.

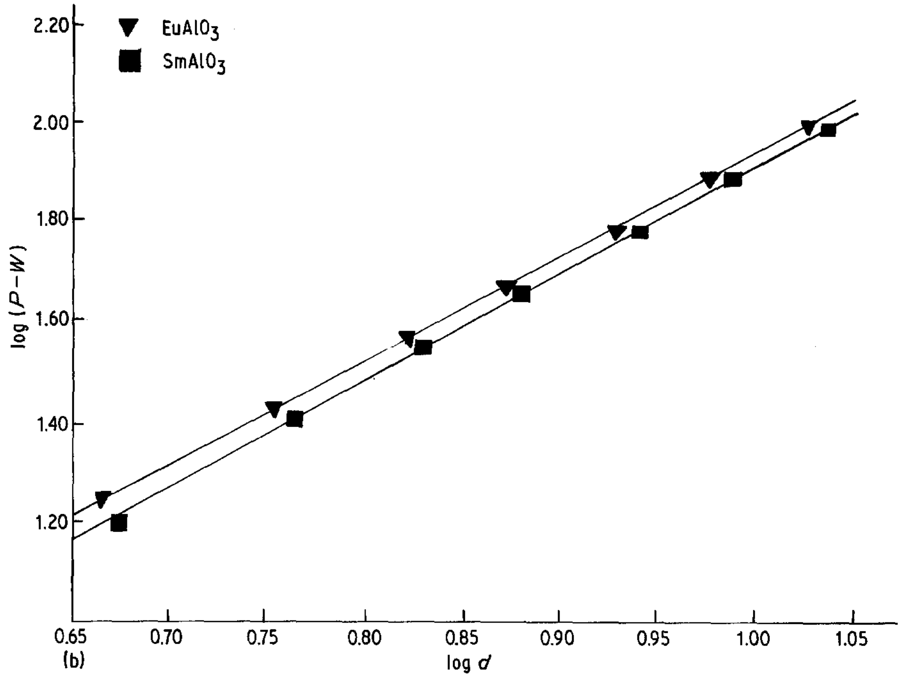


Figure 12 Continued.

tory, University of Oxford. The authors are grateful to Dr G. Garton, of the Crystal Growth Group, Clarendon Laboratory, Oxford for his encouragement in the collaborative research programme. We are thankful to the Head of the Physics department, University of Jammu, for the interest shown. We are also thankful to Professor N. K. Rao for his encouragement.

References

1. J. D. CASHION, A. H. COOKE, J. F. B. HAMKES, M. J. M. LEASK, T. L. THORP and M. R. WELLS, *J. Appl. Phys.* **39** (1968) 1360.
2. J. D. CASHION, A. H. COOKE, M. J. LEASK, T. L. THORP and M. R. WELLS, *J. Mater. Sci.* **3** (1968) 402.
3. J. SIVARDIERE and S. QUEZEL-AMBRUMAZ, *Compt. Rend. Acad. Sci. (Paris)* **B273** (1971) 619.
4. V. R. REGAL, V. G. GOVORKOV and A. F. ZAKATOV, *Zavodsk Lab.* **26** (1960) 243.
5. L. M. BELYAEV, V. G. GOVORKOV, G. F. DOBRZHANSKI, YU. N. MAITYSHER and M. P. SHASKOLSKAYA, "Growth of Crystals", Vol. 6A, edited by N. N. Sheftal (Consultants Bureau, New York, 1968) p. 121.
6. K. J. PRATAP and V. HARIBABU, *Bull. Mater. Sci.* **2** (1980) 43.
7. U. V. SABBA RAO and V. HARIBABU, *Pramana* **11** (1978) 149.
8. M. LAKSHMIPATHI RAO and V. HARIBABU, *Ind. J. Pure and Appl. Phys.* **16** (1978) 821.
9. V. K. NARASIMHA REDDY, M. LAKSHMIPATHI RAO and V. HARI BABU, *Ind. J. Pure and Appl. Phys.* 77 (1979) 806.
10. A. R. PATEL and C. C. DESAI, *J. Phys. D: Appl. Phys.* **3** (1970) 1645.
11. K. SANGWAL, A. R. PATEL, *ibid.* 7 (1974) 203.
12. K. S. RAJU, *Pramana* **8** (1977) 266.
13. A. R. PATEL and H. L. BHAT, *J. Phys. D: Appl. Phys.* **4** (1971) 1998.
14. TOMOZO NISHI KAWA, YASUNORI OKAMOTO and SHIGEKI INAGAKI, *J. Ceramic Soc. Jpn* **91** (1983) 150.
15. A. R. PATEL and S. K. ARORA, *J. Mater. Sci.* **12** (1977) 2124.
16. B. M. WANKLYN, *J. Crystal Growth* 5 (1969) 323.
17. J. W. DAVISON and W. H. WAUGHAN, *Rep. Naval Res. Lab. Prog.* April 10 (1958).
18. P. N. KOTRU, A. K. RAZDAN, K. K. RAINA and B. M. WANKLYN, *J. Mater. Sci.* (1983) to be published.
19. G. Y. CHIN, L. G. VAN UITERT, M. L. GREEN and G. J. ZYDRIK, *Scripta Metall.* **6** (1972) 503.
20. J. R. HOPKINS, J. A. MILLER and J. J. MARTIN, *Phys. Status Solidi A* **19** (1933) 591.
21. G. P. UPIT and S. A. VARCHANYA, *ibid.* **17** (1966) 831.
22. C. HAYS and E. G. KENDALL, *Metallography* **6** (1973) 275.
23. F. KICK, "Das Gesetzder, Proportionalen Winderstande und Science answendung" Leipzig Felix (ed.)
24. F. SCHULTZ and H. HANEMANN, *Z. Metallkde* **33** (1941) 124.
25. C. L. SARAF, Ph.D. Thesis, Maharaja Sayaji Rao University, Baroda, and private communication.

*Received 12 August
and accepted 1 November 1983*