MICROHARDNESS OF GALENA RELATED TO AG-BI-CONTENT, ORIENTATION AND DEFORMATION

HANS PAULY AND HEINRICH SIEMES

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Vickers Hardness Numbers, VHN_{100}, have been determined on oriented cleavage pieces of galenas from Ivigtut, South Greenland, from Mesters Vig, East Greenland, and on fine grained galena from Bunker Hill, USA. The galenas from Ivigtut contain up to 5 % matildite, $AgBiS_2$, in solid solution whereas the galena from Mesters Vig is virtually pure galena. The galena from Bunker Hill was artificially deformed to varying degrees.

Increasing matildite content and increasing VHN show positive correlation as already demonstrated by Lebedeva (1963). VHN-determinations are, however, not usable as an indicator for silver content because VHN also depends on other factors.

The orientation of the sample and of the indentation give rise to variations of up to 20 VHNs in the same galena. Deformation raises VHN; 36% compression was found to increase VHN 20%. Other factors, not identified in this work, also seem to influence the VHN of galena.

Hans Pauly, Mineralogical Institute, Technical University of Denmark, Lyngby, Denmark. Heinrich Siemes, Technische Hochschule, Aachen, West Germany. *January 19th, 1972.*

Inspired by the work of Lebedeva (1963) who showed that an increase in silver content raised the microhardness of galena, it was found of interest to investigate more closely the composition and microhardness of galena from the Ivigtut cryolite deposit in South Greenland. For a long time this galena has been known to contain silver and bismuth, mainly in solid solution.

Even in the preliminary stages of the examination hardness variations were encountered which could not be related to compositional variations. Work-hardening was suspected to cause the rise in microhardness in some cases and in order to assess the influence of previous deformation a series of artificially deformed galenas from Bunker Hill, Kellog, Coeur d'Alene District, Idaho, USA, was added to the material of this examination. In or-

der to get some sort of zero line or base for the examination, samples of very pure galena from the lead-zinc deposit at Mesters Vig in East Greenland were also included in this examination.

Hardness determination

The hardness determinations were carried out by means of a Leitz Durimet Pol. In all cases a 100 g load was applied. Between two and three thousand determinations were made on 50 samples represented by about 100 grains of galena. At least 10 impressions were made in single grains, but 25 impressions were made in single grains from some samples. All grains from Ivigtut and Mesters Vig were cleavage fragments. Most of them were polished parallel with the cube face but in the Ivigtut material grains were also polished approximately parallel with the octahedral face and the rhombododecahedral face. The grains which measured from 2 to 6 mm in diameter, were moulded in Araldite. They were ground with fine carborundum fol-

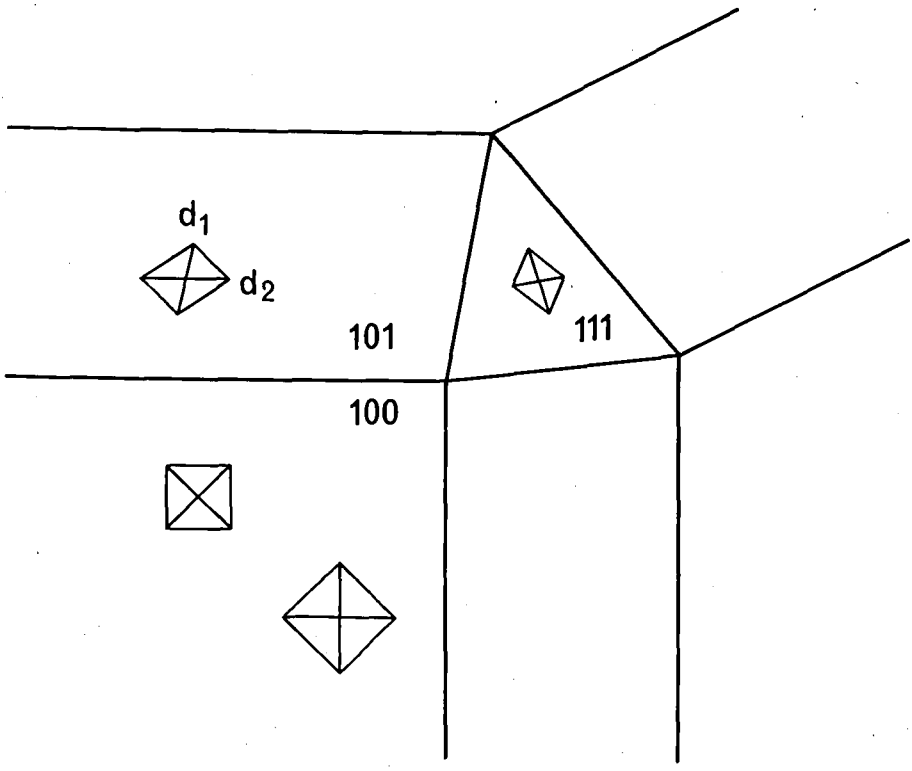

Fig. 1. Orientation of indentations in the examined galena sections.

lowed by diamond, in grainsizes from 15 microns to 1 micron, and finally polished with MgO.

In oriented grains the indenter was oriented according to the crystallographic directions. On the polished cube faces the diagonals of the indentations were placed parallel with the cleavage as given by the borderline of the grain or by cleavage cracks in the surface of the sample. In this way one series of determinations was made. Parallel with such a row of indentations a series of indentations was then made with the diagonals at 45° to the first chosen orientation.

On the octahedral faces the diagonals were places so that one of them was perpendicular to the cleavage, and on the rhombododecahedral faces the diagonals were placed at right angles to the cleavage. Fig. 1 illustrates the orientation of the indentations.

Orientation of samples and of indentations were only accurate to within a few degrees, but it appears that this is accurate enough for the kind of examination, especially taken the nature of the materials in consideration.

Galena from Ivigtut

Galena from the Ivigtut cryolite deposit contains economically interesting amounts of Ag and Bi. During the treatment of the crude cryolite, a galena concentrate is also produced.

Between 1937 and 1964, the average analysis of 44 concentrates sold according to specified contents of Pb, Ag and Bi was: Pb 76.83 %, Ag 0.7361 %, Bi 1.3486 %. These figures give an average Ag/Bi ratio of 0.5458. Assuming Ag and Bi to be present as a solid solution of matildite in the galena the Ag/Bi ratio should be 0.515. The ratio 0.5458 therefore either indicates a surplus of Ag amounting to 0.0410 abs. % or a deficit of Bi amounting to 0.0794 abs. %. The error in such commercial analyses lies well within these values. Calculations of the matildite percentage from the above Ag and Bi contents give:

Matildite based on Ag	2.60% in the concentrate
Matildite based on Bi	2.46% in the concentrate
Average:	2.53% in the concentrate

Recalculation to pure galena gives PbS 97.23 %, matildite 2.77 %. Using the average figure for matildite in galena, a surplus of Ag amounting to 0.02 % is produced. This excess of Ag corresponds well with observations of Ag-bearing minerals different from matildite microscopically included in the galena. Rarely do such inclusions exceed 0.2–0.3 %. Matildite is found

but rarely in galena from Ivigtut in some unusual parageneses, see Ramdohr (1938).

In 1953, a few concentrates showed excess Bi corresponding to the presence of Bi-minerals. The source raw material came from parts of the cryolite mine where the sulphide parageneses contained peculiar Bi-Ag-minerals—berryite and gustavite (Karup-Møller, 1966, 1970). A description of the microscopic inclusions in Ivigtut galenas will be given in a later paper.

Galena samples for the present examination were chosen from about thirty localities within the deposit. These samples cover the parageneses siderite-cryolite (Pauly, 1960) and fluorite-cryolite as well as various mineralised materials from the marginal parts of the deposit. Cleavage fragments (about 1 sq. cm.) were taken from within the galena samples for chemical analysis and for polished sections.

Silver and bismuth analyses were based on atomic absorption spectrophotometry. They showed that silver and bismuth in the samples ranged from nearly zero to about 2 and 6 % respectively. A number of analyses gave results similar to the average values found in the above mentioned concentrates. The wide variation in silver and bismuth content of the samples was interesting but so far no immediate relation to position within the deposit has been established.

Among the analysed galenas from Ivigtut, ten were selected for hardness determinations. They were chosen so as to cover the common paragenesis siderite-cryolite material, the fluorite-cryolite, and various mineralised materials from marginal parts of the deposit. Several cleavage pieces from each sampling area in each sample were used in the chemical analysis. The minimum size of these pieces was about 2 mm. They were carefully inspected in a binocular microscope and only grains where nothing but galena could be seen were used. However, many tiny inclusions were found when grains corresponding to analysed pieces were examined under the ore microscope. Among these inclusions were several silver-bearing minerals. An estimate showed that nearly 0.3 % of the silver content of one sample, containing 1.57 % Ag, should be attributed to included silver minerals. In this sample the silver in solid solution in galena could therefore only be about 1.3 %.

This example illustrates the difficulties involved in relating microhardness to the content of elements in solid solution. The analyses had to be carried out on the samples actually used in the hardness determinations and if possible the analyses had to represent just the area where the indentations were made. Electron microsonde analyses have therefore also been made on the samples used in the microscopic work. As the amounts of silver and bismuth are rather low judged by the possibilities for determination with the

microsonde as a yardstick, and as the interest focuses on the even smaller differences between the samples it was necessary to run as many samples through the microsonde in one series as possible. At the same time it was necessary to obtain silver and bismuth contemporaneously from the same spot. From the microsonde work we obtained the results tabulated in table 1 which also gives the chemical analyses of the samples.

Although variations were observed between galena grains from different areas in the galena mass of the sample, significant variations were not registered within the single cleavage pieces. Several traverses covering 0.3 mm in the polished surfaces were made with the microsonde without detecting variations in silver and bismuth content larger than normal scatter of this type of analysis.

Table 1. Silver and bismuth content in galena from Ivigtut.

Preparate number	Ag - chem.	Ag - sonde 1. series	Ag - sonde 2. series	Bi - chem.	Bi - sonde
77	0.09	0		0.07	0
180	0.45	0		0.05	0
75	0.67	0.66	0.64	1.30	1.35
71	0.70	0.68	0.72	1.35	1.41
89	(–)	*0.85*[1])	0.87	(–)	*1.65*[2])
65	0.87	0.94		1.70	1.75
68	0.93	1.01		1.85	1.94
80	1.35	1.23		2.60	2.58
90	1.35	1.25	1.24	2.60	2.64
61	1.43	1.41	1.22	2.75	2.83

1) Mean of microsonde determinations on the five grains in the polished preparate. For further comments see below and table 2.
2) Calculated from the silver value 0.85 assuming Ag:Bi corresponding to the matildite ration.

Note: Ag determinations in the second column and Bi determinations in the last column have been standardised to the values of preparate number 89 (values italicised).

The agreement between the various determinations is acceptable, but it should be added that an uncertainty of up to 10 per cent relative seems to be indicated through repeat analyses both in the chemical and the microsonde determinations.

The chemical analyses of the single galena samples show the same pattern as the chemical analyses of the concentrates: silver and bismuth occur in proportions close to the proportions found in matildite, but with a slight surplus of silver. The uncertainty in the microsonde analyses prevented further evaluation of this problem. The presence of various silver-bearing minerals occurring as microscopic inclusions in the galena was confirmed through microsonde analyses.

The polished preparate 89, containing 5 grains polished parallel to the cube face, was made from the same galena sample as the preparates numbered 65 and 68. Chemical analyses of galena from this sample indicated silver in amounts from 0.87 % to 1.01 %. A specific series of microsonde analyses on 89 gave, with pure silver as a standard, silver values in the single grains in preparate 89 as shown in table 2 where the VHN of the grains are also tabulated.

Table 2. Silver content and VHN on polished cube face in five grains of preparate 89, Ivigtut.

Grain number	Ag %	VHN 45°to cleavage	s	VHN 0°to cleavage	s	VHN cleavage	s
I	0.83	95.4	9.8	82.7	3.3	89.1	
II	0.85	86.1	11.7	76.9	4.7	81.5	
III	0.84	92.4	5.3	84.1	4.9	88.3	
IV	0.86	95.4	5.5	80.7	6.7	88.1	
V	0.88	95.0	7.5	84.8	5.2	89.9	
IV		36 indentations with 10° between each				88.3	6.2

The five grains show the same silver content; the spread in the values is within the precision of the technique. This content corresponds fairly well with the values obtained on other grains from the sample both by chemical and microsonde methods. It is therefore assumed that the above microsonde determinations giving an average of 0.85 % silver might serve as a suitable reference for the microsonde determinations in other grains. It has further been decided to represent the bismuth content of this sample through a value calculated under the assumption that Ag:Bi is exactly in the ratio found in $AgBiS_2$, matildite. The chemical determination is in agreement with this assumption, although it must be admitted that a slight departure from the exact proportions cannot be ruled out.

The values obtained by using preparate 89 as a basis for the microsonde determinations of Ag and Bi are those given in table 1, columns 3 and 6. These values are used in the following.

In table 2, the VHN values determined as the average of 25 determinations in each grain have also been given. The average VHN of grain IV (obtained through 36 indentations made with 10° rotation of the sample relative to the indenter between each determination) is also given.

Consistency between measurements within the grains appears to be satisfactory. Grain II might have been ruled out because of its very low values. The results would then be 94.6 and 83.1 as the averages for galena in preparate 89. As, however, nothing faulty was found in grain II and the indentations appear satisfactory, there is no reason for doing so other than the low values which result in a poor fit in the VHN/Ag diagram (fig. 2). The low

values are only about 6 VHN below the average and this would not seem to justify their ommission.

In table 3 all VHN values on galenas from Ivigtut have been brought together. Preparate 85 represents average values obtained on galena from Mesters Vig. In the table are given the high and the low values found on the cube faces. These values are averages determined from 10 or 25 indentations in each of several grains. The number of grains and total number of indentations for these averages have been noted in the table. The VHN values obtained on (110) faces are given specifically for each diagonal, d_1 and d_2. The differences between the two diagonals have been given, in microns, in order to illustrate the variation. Finally the VHN found on (111) is also given. It can be seen that this VHN value is higher than the value obtained on the (110) faces. It may be lower than the average found on (110) but this is not always the case. One might conclude that the lowest possible VHN value in galena is represented by the low value found on (110).

In fig. 2, the VHN of the cube faces have been plotted against the Ag-content of the galenas. The Ag- and Bi-free galena from Mesters Vig is

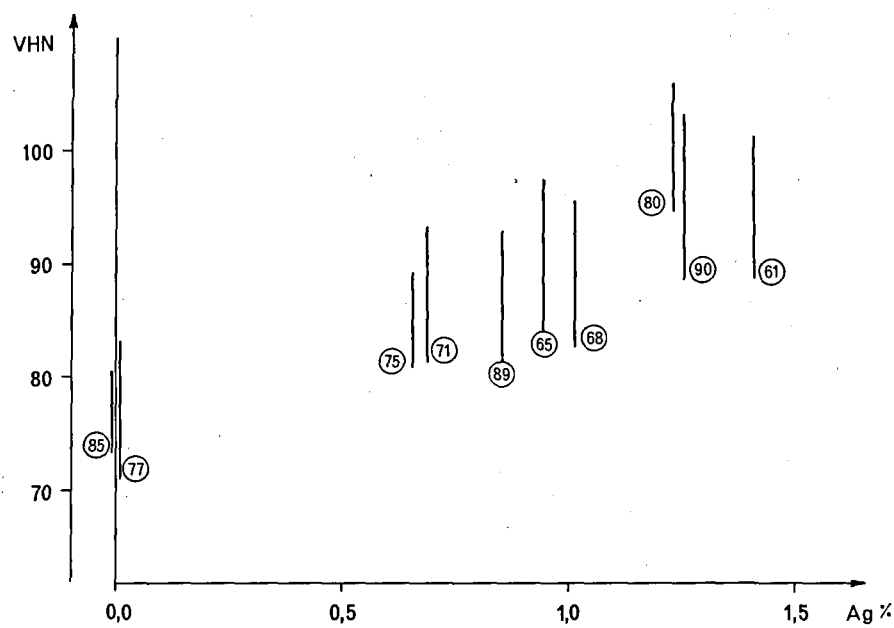

Fig. 2. Ag-content of galenas plotted against VHN_{100}-values. Ends of bars mark average of highest and average of lowest values obtained on (100). Numbers in circles indicate sample number. No. 85 is galena from Mesters Vig, the others are from Ivigtut.

Table 3. VHN of galena in relation to crystallographic orientation and Ag-Bi content.

Prep. no.	VHN-averages and »s« on crystal faces (100) 45°	s	(100) 0°	s	Aver.	(110) VHN d_1	(110) VHN d_2	d_1-d_2 μ	(111)	Number of grains and determinations	Ag-sonde	Bi-sonde	Matildite	a_0 (400) in Å
85	80.5	3.9	73.3	4.4	76.9					5 135	0.00	0.00	0.0	5.936
180	81.2		72.1		76.7					2 20	0.00	0.00	0.0	
77	83.2		71.3		77.3					7 70	0.00	0.00	0.0	5.940
78						68.4	71.4	1.11		1 10				
79									70.9	1 10				
75	89.5		80.9		85.2					6 60	0.66	1.35	2.3	5.933
74						70.1	74.3	1.47		1 10				
76									79.0	1 10				
71	93.6		81.5		87.6					6 60	0.68	1.41	2.4	5.934
73						76.8	79.3	0.77		1 10				
72									80.9	1 10				
89	92.8	8.0	81.8	5.0	87.3					5 128	*0.85*	*1.65*	3.0	
65	97.5		84.5		91.0					6 60	0.94	1.75	3.3	
67						83.5	86.9	0.92		1 10				5.927
66									88.3	1 10				
68	95.8		82.9		89.4					7 70	1.01	1.94	3.6	
70						79.3	83.7	1.39		1 10				
69									83.0	1 10				
80	106.2		95.0		100.6					2 20	1.23	2.58	4.3	
81						86.0	91.0	1.32		1 10				5.924
82									87.2	1 10				
90	103.5	5.7	88.9	6.4	96.2					5 125	1.25	2.64	4.4	
61	101.4		88.9		95.1					6 60	1.41	2.83	5.0	5.919
63						82.3	89.9	2.02		1 10				
62									89.6	1 10				

Note: preparate no. 85 is from Mesters Vig, the others from Ivigtut.

represented in the figure by the average values obtained from samples 85 and 85A.

Plotting of the unit cell dimensions against matildite content in the galenas seems to give too abrupt a decrease in size with increasing matildite content when compared with the data on homogeneous solid solutions given by Craig (1967). It should be added that our results have an uncertainty of about ± 0.003 Å.

From fig. 2, the general increase in VHN with rising Ag content is clear. As the ends of the bars in the figure give values of maximum and minimum VHN on the cube faces it is seen that these values are correlated in a similar way to the Ag content. Similar features are produced when the VHN of the other crystal faces are plotted against Ag content even though these VHN values are obtained on preparates different from those with polished cube faces.

In all cases it is obvious that breaks occur in the plots. These breaks may indicate properties in the galena samples unrelated to composition or preparation technique. It is, however, impossible to point to definite causes for these variations. Possibly the breaks might be attributed to errors in the hardness determinations but such an explanation may not fully cover the fall in hardness indicated by the two last samples having the highest silver-bismuth contents.

The uncertainties in the determination of the silver and bismuth also influence the results and from the present study one can only conclude that a broad correlation exists between microhardness and silver-bismuth content.

Galena from Mesters Vig

Mesters Vig in East Greenland was the site of lead-zinc mining from 1953 to 1961. A mineralised fault system in Permian sandstone carried galena and sphalerite in a quartz gangue with some baryte. Other minerals were very scarce. The mineralisation is thought to be of Tertiary age. A description of the deposit has been given by Bondam & Brown (1955).

The concentrates from the mine were very low in silver, bismuth and other minor elements. Mr. E. Hintsteiner, geologist at Nordisk Mineselskab A/S, reported (from the company's archives) that a concentrate from September 1959 contained:

Bi 0.001% As 0.03% Sb tr., Ag 0.0113%

As the galena from this mine occurred in rather coarse crystalline aggregates the material was regarded as a suitable base for comparison in the present study.

From an aggregate, with centimetre-sized cleavage faces, two fragments 10 to 15 millimetres across were chosen. After preparation and polishing the first piece appeared as three grains separated by partly filled cracks, whereas the second piece broke in two, one part being composed of two individuals. The two polished samples thus each contained three distinct areas of galena. Closer inspection under the microscope showed all grains to be built up of wedgeshaped sub-individuals obviously representing slightly broken or bent parts of an originally homogeneous crystal. The orientation of the grains thus varied from area to area. The hardness impressions were therefore mainly oriented according to the directions of cleavage cracks and pits in the surface. Sufficiently large areas were present in all six grains to allow about 25 impressions to be made within the same crystal orientation. Distances between impressions, and between impressions and grain boundary, were always greater than 0.2 mm. The size of impressions was about 0.05 mm.

The results and average of the VHN-determinations in the two samples are given separately in table 4.

Table 4. VHN of galena from Mesters Vig.

Preparate number	VHN 45°to cleavage	s	VHN 0°to cleavage	s	Numbers of grain	Numbers of determinations
85	79.5	3	72.2	4	3	75
85A	82.2	4	74.2	4	3	60
Average	80.53	3.87	73.29	4.39	6	135

Histograms illustrating the measurements are given in fig. 3. The distributions show a slight skewness towards lower VHN for both directions. This seems to be the case in all series of this work. It may be the result of polishing of a mineral with such a good cleavage as galena. The mechanical treatment together with the cleavage creates possibilities for "soft spots" in the preparate.

The overall appearance of the Mesters Vig ore indicates that the ore body has been subject to later deformations, e.g. the above mentioned wedge shaped sub-individuals. This brought up the idea to look for relict work-hardening in the galena.

Sample 85A was placed up-side-down on a glass plate and heated to 110°C for 24 hours in an incubator. As the polished surface looked quite fresh after this treatement, ten hardness determinations were carried out close to the original impressions. The average was very close to the earlier determinations and the sample was again heated to 110°C now for a week. All in all the sample was thus annealed for 172 hours at 110°C. A few impressions were afterwards made in a still good-looking area and they

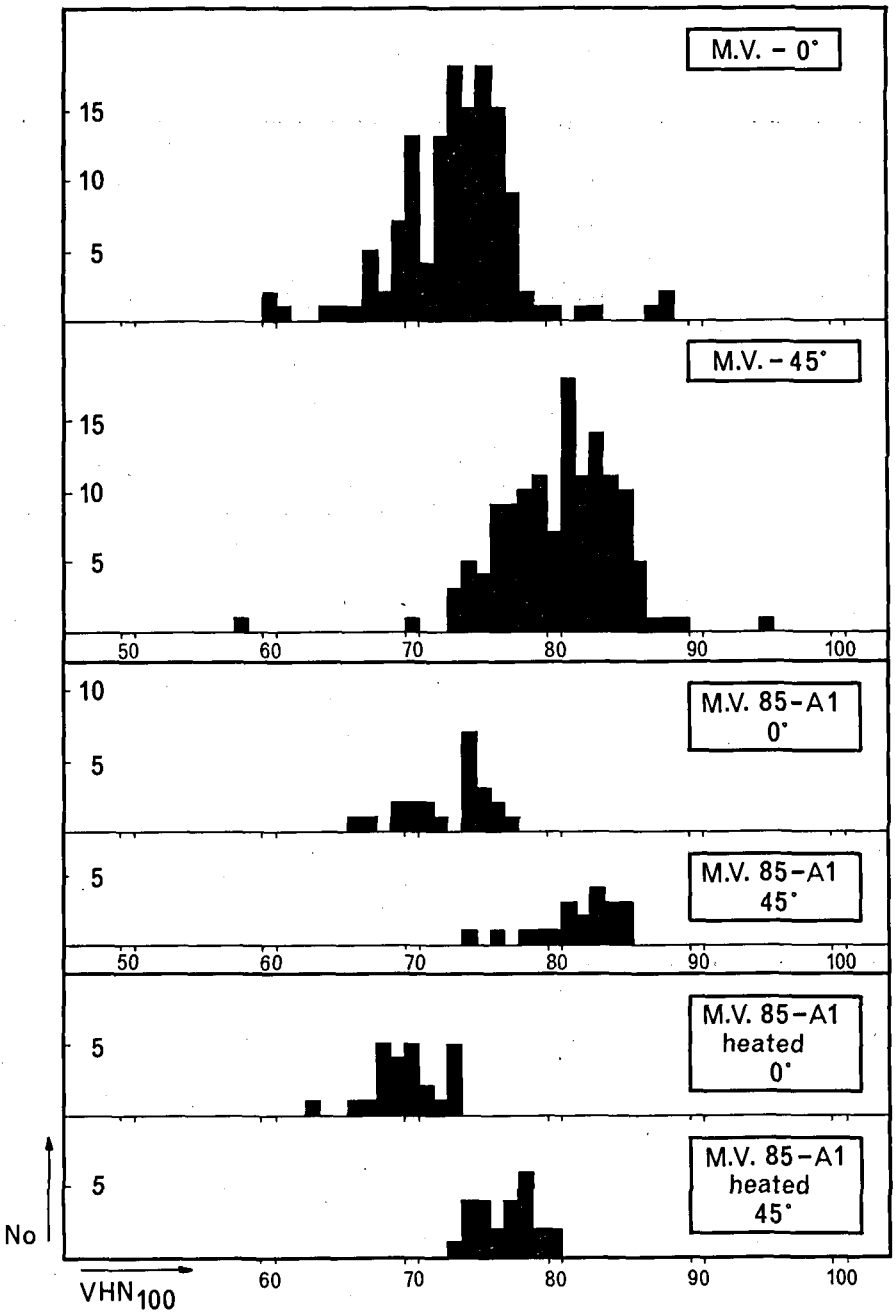

Fig. 3. Histograms in upper two figures illustrate hardness determinations on (100) of Mesters Vig galena (samples no. 85 and 85A). M. V. 0° and M. V. 45° give VHN_{100} with indenter diagonals at 0° and 45° respectively against the cleavage direction. Histograms in lower four figures give VHN_{100} on a single grain from Mesters Vig 85A–1. M. V. 85A–1 0° and 45° give low and high values of (100) before heating, and M. V. 85A–1 heated 0° and 45° gives VHN_{100} after heating (110° C for 172 hours).

showed clearly lower VHN values than before. The sample was repolished and 25 determinations were made in each of the two directions in the cube face. The values obtained are given in Table 5 together with the values originally found on the same grain.

Table 5. VHN on Mesters Vig galena and VHN on heated and on etched grains of the same samples.

	45° to cleavage		0° to cleavage		Numbers of
	$\bar{X}$	s	$\bar{X}$	s	determinations
Mesters Vig total	80.53	3.87	73.29	4.39	135
MV 85A–1	81.68	2.91	72.62	2.90	21
do., do. heated	76.66	1.93	69.54	2.35	25
MV 85–1	81.34	2.64	72.60	2.55	25
do., do. etched	81.18	2.51	74.03	2.80	25
MV 85–2	76.29	2.08	70.80	3.05	25
do., do. etched	79.02	2.93	71.74	2.89	25

The histograms in fig. 3 illustrate the hardness determination on this grain in the two directions on the cube face before and after heating. The lower value for the heat treated sample was confirmed through a t-test whicb showed that the results were significantly lower than both the results obtained on the untreated grain and the results from the total Mesters Vig material.

One might suspect repolishing (involving the use of diamond paste from 7 μ downwards) to improve the sample surface by minimising the thickness of a disordered surface layer. To test this, the other Mesters Vig sample was therefore etched with nitric acid in alcohol and repolished. From the diameter of the remaining parts of the earlier hardness-indentations it was judged that a layer of close to 4 microns had been removed.

A new series of hardness measurements was carried out on the etched sample. The results obtained are pictured in fig. 4 in the form of histograms and the values found are given in table 5. From this it is seen that the two measured grains in the etched sample both gave slightly higher hardness values than before etching. This was again confirmed through a t-test which at the same time showed that the etched grains gave hardness values not differing significantly from the results of the total Mesters Vig galena.

The rise in hardness found on the etched grains may be explained by assuming that the original polishing has not been careful enough and this fault has been diminished through etching and repolishing. This is a procedure often recommended in connection with the preparation of metal surfaces where it is essential to get rid of the influence from faulty polishing.

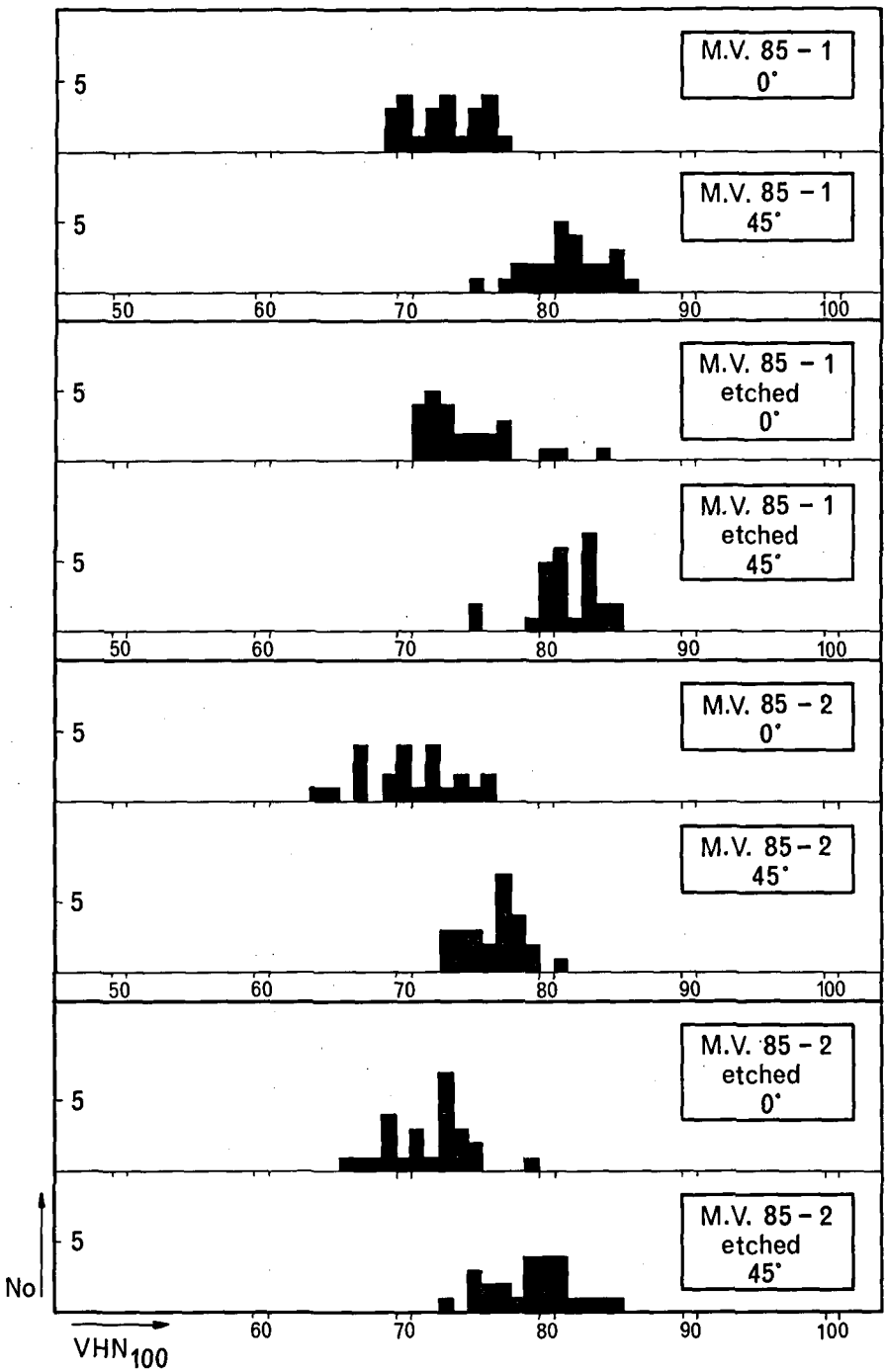

Fig. 4. Histograms giving VHN_{100} on etched grains of Mesters Vig sample no. 85. For comparison VHN_{100}-values of the same grains unetched are also given.

Artificially deformed galena

Artificially deformed galena from Bunker Hill Mine, Kellog, Coeur d'Alene District, Idaho, USA, has been tested for microhardness in order to elucidate hardness variations in relation to degree of deformation and other deformation characteristics.

The Bunker Hill galena appears as a crystalline aggregate composed of grains about 1 mm in diameter. Microscopy indicates the presence of bournonite and boulangerite. They represent the bulk of disseminated inclusions; tetrahedrite and sphalerite are much rarer. The grainsize of these inclusions ranges between 10 and 150 μ. X-ray fluorescence analyses showed a content of 1550 ppm Ag and 1850 ppm Sb. The specific gravity of the galena aggregate was found to be close to the theoretical value of galena, 7.6 g/cm^3.

Although the galena ore of the Bunker Hill Mine certainly had been at some time more or less naturally deformed, the regular polygonal shape of the grains permits the conclusion that later recrystallisation has also occurred, as has been proved on similar naturally deformed galena (Siemes, 1961, 1964; Stanton & Gorman, 1968).

X-ray examination of the galena before experimental deformation shows that there is a preferred orientation of the lattice in relation to the selected orientation of the axis of the cylindrical specimens. This initial fabric shows a maximum with an intensity ratio[1]) of 1.61 ± 0.35[2]) for [200] and a minimum with ratio of 0.79 ± 0.20 for [111] parallel to the axis of the specimens. The intensity ratio for [220] is 1.02 ± 0.30. This fabric is penetrative for the whole block, but there are very strong local deviations. In fig. 5 are given, as an example, the intensity profiles of one specimen of the undeformed material. The intensity ratios of [200], [220], and [111] in the direction of the axis of the specimen (pole distance 0°) are different from the mean intensity ratios.

For the deformation experiments, 47 cylindrical specimens were drilled out of a galena block measuring $12 \times 10 \times 8$ cm. Each cylinder was 12.7 mm in diameter and 25.4 mm in length. The copper jacketed specimens were deformed by axial compression under confining pressure by means of an apparatus of the v. Kármán-type. The confining pressure was varied between atmospheric pressure and 3000 bars. The largest strain which could be attained without leakage of the copper jacket was 36.9 %.

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1. For details about preparing and use of intensity profiles and intensity ratios see Siemes 1966 or 1970, and Baker, Wenk and Christie 1969.
2. This is a mean intensity ratio calculated from measurements on 10 specimens and the absolute value of the standard deviation.

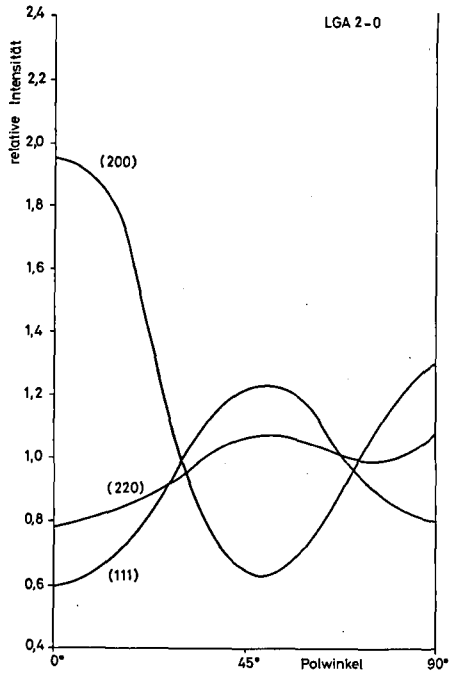

Fig. 5. Intensity profiles of undeformed galena of the series LGA 2.

Stress-strain curves (for details see Siemes, 1967 and 1970) reveal that, at low confining pressures up to 100 bars, the galena behaves in a brittle manner. The specimens show extension and shear fractures. Between 200 and 400 bars the specimens deform mostly by ductile faulting. Above 400 bars confining pressure uniform flow occurs distributed over the whole specimen. According to Handin & Hager (1957) flow under these test conditions may be divided into gliding flow (intracrystalline) and cataclastic flow (intercrystalline), which will be pointed out later.

Stress-strain curves of tests performed under the same conditions generally lie close together, but sometimes deviate considerably. These deviations reflect the variation of the initial fabric of the different specimens.

Twelve specimens deformed by uniform flow were used in the determination of hardness. In addition to these a sample of the undeformed galena was tested for hardness.

As the Bunker Hill galena occurs as millimeter sized grains no attempt was made to carry out hardness tests in oriented crystalfaces. In each sample, polished perpendicular to the cylinder's axis, 25 indentations were made and measured. As might be expected, rather great differences were often found between the diagonals of the single impressions. As appears from table 6 in spite of these differences VHN values determined separately for each diagonal were very close to each other.

Differences in VHN as calculated from the one or the other of the two diagonals may indicate preferred orientation in the galena where the indentations have been made.

Table 6. VHN and deformation characteristics of the LGA-2 series.

No.	VHN $\bar{X}$	s	VHN of $d_1 - d_2$	Confining pressure in bars	Maximum diff. stress in bars	Maximum strain in %
N–5	82.65	4.67	÷0.3	–	–	–
9	83.11	7.14	0.4	500	1997	13.2
7	91.29	5.71	5.2	500	2027	19.4
8	92.19	7.27	÷0.4	500	2009	24.3
10	88.99	8.39	1.2	1000	2483	13.3
12	95.60	5.51	÷2.6	1000	2629	17.7
11	96.72	7.03	2.3	1000	2636	24.0
18	87.78	8.74	2.6	2000	3082	15.1
17	92.47	7.36	2.0	2000	3202	18.0
16	94.02	8.05	2.5	2000	3085	23.7
24	89.92	7.70	1.2	3000	2830	15.0
23	93.91	6.90	0.4	3000	2965	21.0
33	98.45	6.52	÷3.8	3000	2789	36.9

Taking into consideration the hardness anisotropy of galena one might ask what the average VHN represents. Young & Millman (1964, fig. 3) give VHN on different crystallographic faces of a galena from Harz in Germany. Their results can be summarised as follows:

On natural cleavage faces (100):

45° to the cleavage	parallel to the cleavage
77.5	69.0

On polished faces:

(110) 45° to the cleavage	(111) 15° to the cleavage
68.5	63.0

Average on (100) is thus 73.3; total average on these galena faces is 69.5.

In the examination of the VHN of (100) cleavage faces on galena from Ivigtut one of the samples was tested by 36 determinations within the same area, turning the sample 10° between each indentation.

The average of these 36 determinations (88.3) was practically the same as the average (88.1) of two series of indentations which were set parallel to the cleavage and at 45° to the cleavage.

With this in mind it seems reasonable to regard the average VHN of galena as a hardness value close to the VHN on the rhombododecahedral face or the minimum found on the cube faces. The range in hardnesses

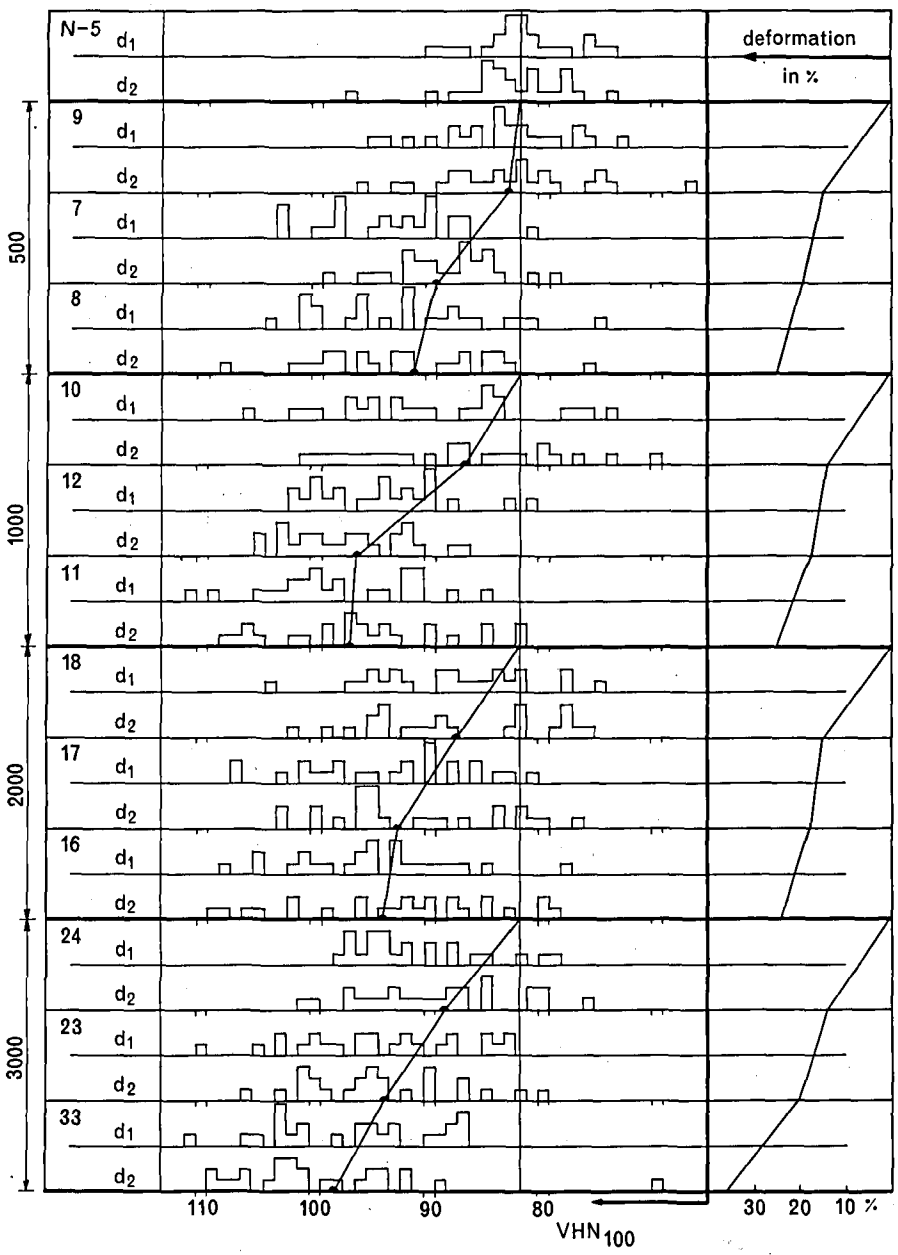

Fig. 6. Galena from Bunker Hill LGA 2. Histograms of VHN_{100} determined separately for the two diagonals of the indentation. The first two rows are results obtained on undeformed galena. The next four series represent galena deformed at increasing confining pressure. Within each series results from three deformation stages are given. For each sample average VHN_{100} is marked. In each series these averages are connected with a line illustrating increasing hardness with increasing deformation. To the right a corresponding curve illustrate deformation within each series.

found on the various crystal faces in the examination of the Ivigtut material corresponds well with the values given by Young & Millman. Their VHN from the octahedral faces represent their lowest values on galena but this is for some reason not the case in the Ivigtut material. It does not look as if this is only a matter of differences in orientation of the indenter diagonals, which we have oriented perpendicular to one of the cleavage directions whereas Young & Millman set it at 15° from the cleavage direction.

Concerning the VHN of the undeformed Bunker Hill galena it might be remarked that the value seems rather high when one considers the silver content of this galena. This was found to be 0.15 % and this value was also found by microsonde determinations. As the bismuth content is very low one might suspect that this type of silvercontaining galena is not comparable with a galena where the silver content is connected with a content of bismuth corresponding to dissolved matildite.

In order to illustrate relations between microhardness and variation in the deformations tests, the histograms in fig. 6 have been set up. Here the VHN for each preparate has been given specifically for each of the two diagonals of the indenter d_1 the vertical and d_2 the horizontal diagonal. Differences in the two diagonals correspond to hardness anisotropy of the measured grain. For each grain the average is plotted. In the four series of deformation tests these averages have been connected with a line showing the variation in microhardness through the series. For each series the deformation expressed as deformation percentage has likewise been plotted and the points for each sample have been connected to show the variation in deformation through the series. One gets a rather good picture of the correspondance between microhardness and deformation within the series.

Intracrystalline reorientation of the galena lattice connected with the deformation process tends to favour an orientation in the deformed samples so that [110] becomes parallel with the axis of the main stress, as shown in Fig. 7.

In order to elucidate further the relations between microhardness, preferred orientation and deformation characteristics a mathematical analysis of the obtained data has been performed using programs developed by Good (1964), Sampson & Davis (1966) and Miesch & Connor (1968).

The deformation experiments on galena are carried out with confining pressure and strain as independent variables. Interdependent variables are 1) the strength (stress) as measured during the test 2) preferred orientation 3) indentation hardness.

In order to compare the behaviour of the three dependent variables it is necessary to plot them as isolines in a coordinate system with strain (X) on the ordinate and confining pressure (Y) on the abscissa. The sometimes very strong local variations of the initial fabric and thus the variations in

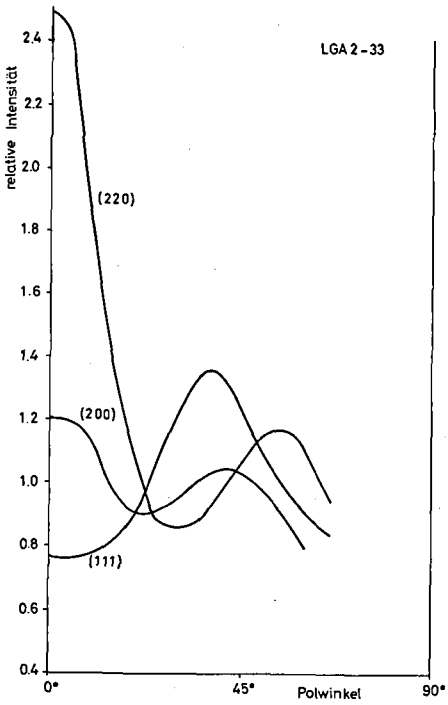

Fig. 7. Intensity profiles of deformed galena of the series LGA 2 (3000 bars confining pressure, 36.9% strain).

strength and probably in indentation hardness, did not permit isolines to be drawn by simple interpolation methods. An analysis has been tried first by interpolating the measured data by polynoms first to fourth degree. More successful were the calculations using 38 polynomial terms as presented in a stepwise regression program by Miesch & Connor (1968). The terms of the regression equations of the measured data selected on a 0.05 and 0.01 probability level, are the same. Table 7 gives the selected terms as described in the program by Miesch & Connor (1968), the multiple regression coefficients, and the percentage of total sums of squares of dependent variable explained.

The intensity ratios of the (111)-, (200)-, and (220)-reflections of two parallel sections through the center of 22 deformed specimens were used as a measure of the preferred orientation of the lattice. Figs. 8, 9 and 10 give the contoured surfaces of the (220)-, (200)-, and (111)-intensity ratios respectively. Because of the strong local variations of the initial fabric the multiple regression coefficients at least for (200) and (111) are rather low, but the interpolated surfaces seem to give a reasonable relationship between the independent and dependent variables. The (220)-ratios rise rapidly from about 1.0 to about 2.9. The change in orientation depending on increasing confining pressure and increasing strain is significant because it

Table 7. The selected terms according to *Miesch* and *Conner*, the multiple regression coefficients and percentage of total sums of squares of dependent variable explained.

Q = 0.01 / Q = 0.05	strength (bar)	(111)	(200)	(220)	VHN
Correlation coefficient	0.9986	0.560	0.492	0.881	0.827
Percent of total sums of squares of dependent variables explained	99.719	31.38	24.19	65.84	68.37
1 constant	$\div 1.720 \cdot 10^{1}$	$+8.018 \cdot 10^{-1}$	$+1.624$	$+9.885 \cdot 10^{-1}$	$+8.097 \cdot 10^{1}$
2 X	$\div 9.878 \cdot 10^{-2}$				$+5.329 \cdot 10^{-1}$
3 Y	$\div 1.749 \cdot 10^{1}$				
8 X^2Y	$+1.758 \cdot 10^{-3}$			$+3.582 \cdot 10^{-4}$	
9 XY^2	$\div 4.419 \cdot 10^{-2}$				
12 X^3Y	$\div 6.283 \cdot 10^{-5}$				
13 X^2Y^2	$+8.495 \cdot 10^{-4}$				
17 X^4Y	$+9.599 \cdot 10^{-7}$				
18 X^3Y^2	$\div 1.320 \cdot 10^{-5}$		$\div 1.182 \cdot 10^{-6}$		
20 XY^4	$+1.193 \cdot 10^{-3}$				
21 Y^5	$\div 6.080 \cdot 10^{-2}$				
22 $\sqrt{X}$				$+7.585 \cdot 10^{-2}$	
23 $\sqrt{XY}$	$+8.380 \cdot 10^{-1}$	$\div 2.493 \cdot 10^{-2}$			
29 e^{2y}	$+2.534 \cdot 10^{-2}$				
30 log X	$+5.809 \cdot 10^{-1}$				
31 log Y	$\div 4.284 \cdot 10^{1}$				
33 log X log Y	$+3.844 \cdot 10^{-2}$				
34 $\log Y^2$	$\div 4.324 \cdot 10^{1}$				
35 X^{-1}	$+1.711 \cdot 10^{-28}$				
38 $(XY)^{-1}$	$\div 6.026 \cdot 10^{-30}$				
39 Y^{-2}			$\div 1.108 \cdot 10^{-1}$		

greatly exceeds the range of the (220) intensity variation of the undeformed specimens. The (200) ratios vary between 1.6 and 1.0. The change of intensity is only significant in the upper right corner of fig. 9 and indicates a decrease of the (200) alignment with axis of compression depending on increasing confining pressure and increasing strain. The significance of decrease of the (111) ratio from 0.8 to 0.54 with increasing confining pressure and increasing strain is low. The low decrease should be expected because of the alignment of [200] with axis of the specimen before and the alignment of [220] with the axis of compression after deformation.

The contoured surface of fig. 11 shows that strength increases with increasing strain and increasing confining pressure. In an area from 1700–2400 bars confining pressure and 20 %–38 % strain there is a region of

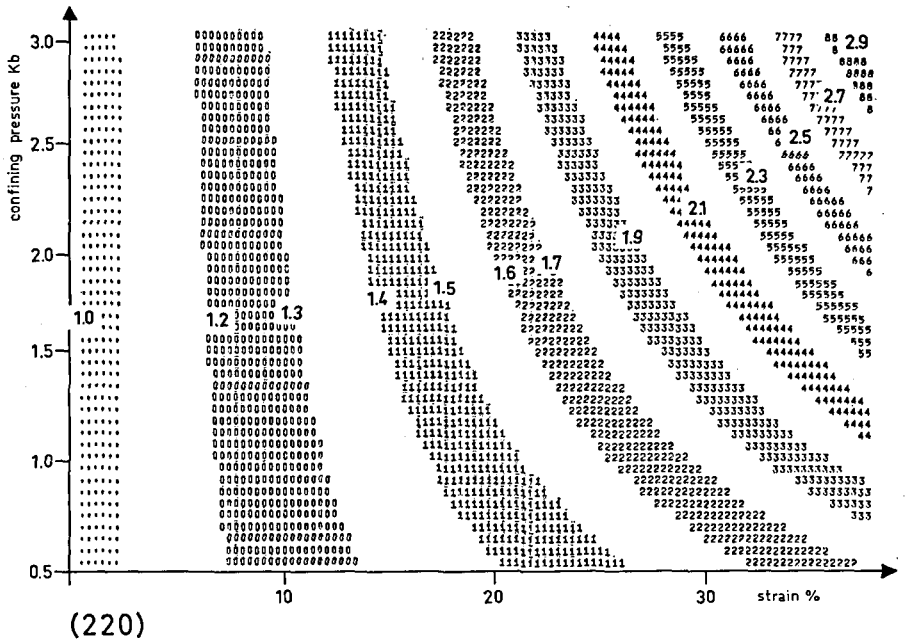

Fig. 8. Contoured surface of the (220) intensity ratios of the deformed galena (22 specimens) of the series LGA 2 dependent on strain (x) and confining pressure (y) computed by stepwise regression.

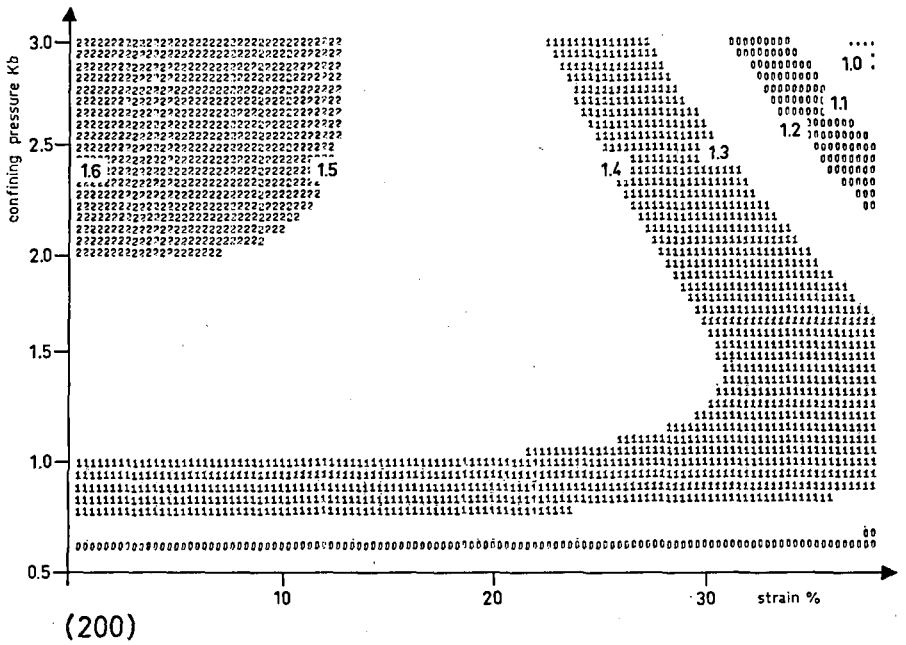

Fig. 9. Contoured surface of the (200) intensity ratios of the deformed galena (22 specimens) of the series LGA 2 dependent on strain (x) and confining pressure (y) computed by stepwise regression.

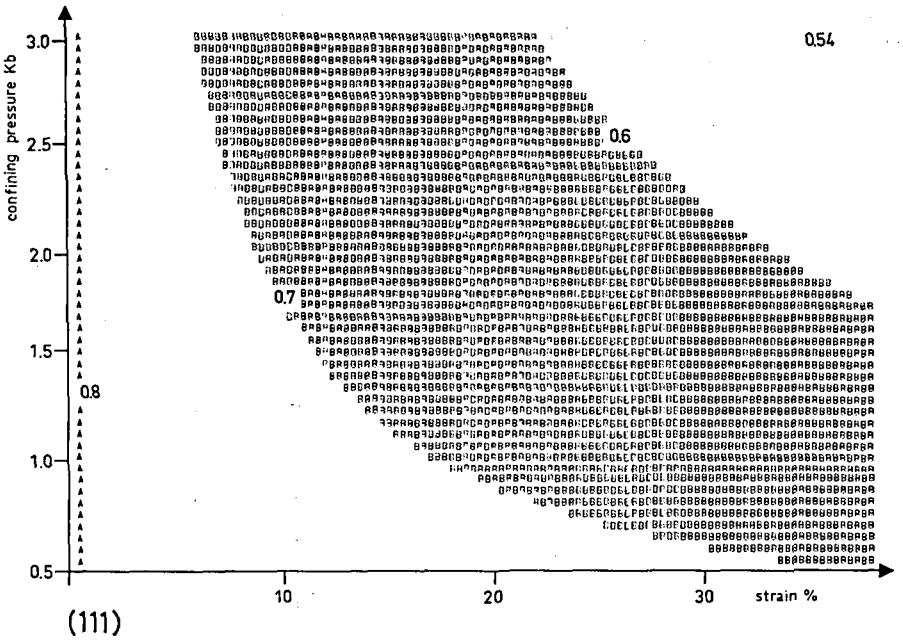

Fig. 10. Contoured surface of the (111) intensity ratios of the deformed galena (22 specimens) of the series LGA 2 dependent on strain (x) and confining pressure (y) computed by stepwise regression.

maximum strength of about 3000 bars (area with digit 5 on fig. 11). The increase in strength is affected by intracrystalline gliding which is connected with strain hardening and reorientation processes of the lattice on the one hand and on the other hand with intercrystalline flow which is very much affected by confining pressure (Lyall & Paterson, 1966).

At low confining pressure (500 bars) the intercrystalline mode of deformation is dominant over the intracrystalline mode. The result is a rather low change in orientation of the lattice and only low strain hardening.

Above about 1500 bars confining pressure the intracrystalline mode of deformation becomes predominant. The faster increase of the intensity ratio of the (220)-reflection is connected with stronger strain hardening than before. The change of the (200)-ratios is not yet significant and it is assumed that the galena grains with this orientation contribute very much to the strength of the specimens. Galena crystals with an orientation of [100] more or less parallel to the axis of compression are of high strength because of the zero resp. very low resolved shear stresses in (100) [110] gliding systems, which has been proved in compression tests on single crystals by Lyall & Paterson (1966).

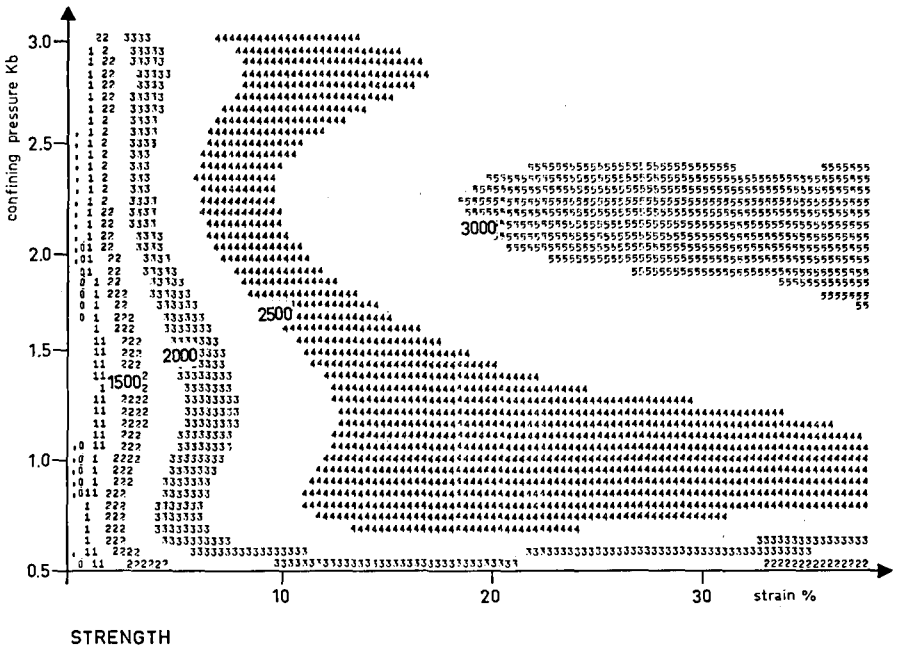

Fig. 11. Contoured surface of the strength of galena of the series LGA 2 dependent on strain (x) and confining pressure (y) computed by stepwise regression from 6 mean stress-strain curves.

With further increasing confining pressure the (220) ratio increases faster with increasing strain. Strain hardening should be more important than before, but above 2500 bars confining pressure the strength of the specimens becomes lower. This is probably due to a faster reduction of the crystals with the [100] orientation. The decrease of the (200) ratio which becomes significant at high confining pressures and high strains seems to confirm this assumption. Probably a change in the mechanism of intracrystalline deformation occurred and the reduction of the strong [100] orientation is more effective than the strain hardening by slip. Lyall & Paterson (1966) showed that the [100] orientation is capable of twinning.

The contoured surface of fig. 12 reveals that indentation hardness depends only on strain. With increasing strain from 0 to 38 % hardness increases from VHN 81 to VHN 101, that is about 25 %. This relationship is not yet well understood. Assuming that indentation hardness is dependent on strain hardening and orientation of the crystals one would expect some dependency on confining pressure, because both are varied by confining pressure and strain. It seems reasonable that several diverging factors are interferring in such a way, that indentation hardness seems to be only dependent on strain.

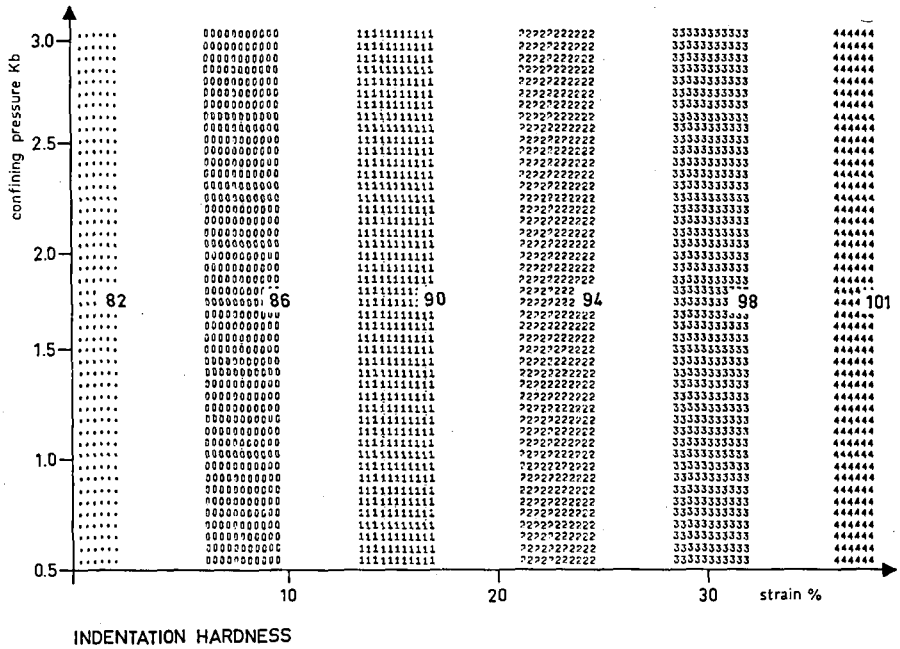

Fig. 12. Contoured surface of the indentation hardness of the deformed galena (12 specimens) of the series LGA 2 dependent on strain (x) and confining pressure (y) computed by stepwise regression.

Microhardness of Galena

Apart from the more or less regular relations between microhardness and 1) crystallographic orientation, 2) amounts of solid solutions and 3) work-hardening from known deformations, the present examination has shown variations in microhardness which could not be traced to specific sources. Some of these could, however, be eliminated through renewed polishing.

Several of the examined samples were plastic mounts carrying several grains from the same spot in the galena sample. In each grain were made 10 —or 25—indentations. In the samples containing polished cube faces two series of indentations were made, one parallel to the cleavage direction and the other at 45° to the cleavage direction. The results of indentation series were averaged and these averages from the different grains in the polished sample usually showed no greater divergences than did the single measurings. In a few cases, however, a single grain gave results greatly differing from the other grains of the sample.

In the preparate 71 the cube faces gave 93.6 and 81.5 in average of 6 grains with variations from 90.0 and 80.5 to 95.5 and 86.5. One grain gave,

however, 74 and 67. The impressions were acceptable so the only reason for rejecting this grain was the extreme low values it gave compared with the other grains from the sample.

In sample 77 seven grains gave the following averages: 83.2 and 71.3 on the cube face. The eighth grain gave as averages of 10 impressions 54 and 45. Again this grain was excluded from the average mainly on its comparatively low value.

Sample no. 180 was regarded with great interest at first because the chemical analyses gave 0.45 % silver but only 0.05 % bismuth. The hardnesses of this sample (averages of 10 determinations) gave 71.0 and 64.8 on the cube face. Interestingly, the microsonde analyses revealed no silver and no bismuth within the galena; all silver occurs in inclusions (of freibergite). This pure galena gave extremely low VHN values, lower than values reported in the literature and lower than the other silver-free samples examined. The sample was repolished; and also a new cleavage piece from the same sample was selected and polished very carefully. Careful inspection during polishing showed that rounded cavities in the sample, which might have been break-outs of the galena, were actually genuine holes or vacuoles cut open through the preparation process. The repolished sample gave VHN 83.1 and 74.2; the new sample gave 79.4 and 70.0. The original results on the first sample were obviously too low. In the preceding table 3 we have taken the average of the two grains but it is certainly a question whether we should have discarded also the results from the new preparate. The results it gave were however only lower than the results on the repolished sample by an amount corresponding to the usual spread between measurements and between grain averages.

Our results clearly indicate that a few measurements on a single grain, even the recommended 10 to 15 measurements, do not guarantee the result and this cannot be helped simply by inspecting the impressions. In the above cases the impressions were nice looking except for some of the impressions in sample 71 where sinusoidal contours were occasionally seen. They were, however, not so deformed as to prevent measuring. What should be added and strongly underlined is that these impressions with hidden faults occurred in both series. The series measured with diagonals parallel to the cleavage gave low values corresponding to low values in the series where the diagonals were set at 45° to the cleavage. Within these low series the single measurements also showed the normal spread.

With this experience in mind, it is difficult to accept the statement by Stanton & Willey (1970) that "Specimens giving *minimum* mean hardnesses are likely to yield better approximations to "true" hardnesses".

In the cases mentioned above one might look for an explanation in some sort of "blading" occurring in the samples which were polished parallel to

the cubic cleavage of the galena. Such a "blading" might be enhanced through the existence of liquid-filled vacuoles where the gas pressure perhaps in co-operation with the polishing produced an extraordinary submicroscopic set of cleavage planes through the grain. All in all this seems to indicate that several grains should be studied when one wish to determine the hardness of a galena. Nothing much is gained from increasing the number of impressions above 10 to 15 in a single grain. The number of grains to be studied might be between 5 and 10.

From the above, it is clear that this discussion involving only free single grains of the mineral under examination differs greatly from the practical situation where one wishes to use hardness determinations in identification work on polished ore samples and generally in the study of composite samples. The "moulded in" character of the individual grains in such samples might give a certain protection from the discussed faults but also here one should at least be very careful when judging the results and, of course, several grains should be examined before the result is accepted.

The results of this study seem to corroborate strongly the earlier published great dependency of the microhardness on the crystallographic orientation of the mineral. Young & Millman found differences on the cube face amounting to about 8.5 VHN. The difference between their highest and lowest value on a Harz galena was 14.5. Their average hardness on the cube face was 73.3. This value is somewhat lower than our values on the silver-free Mesters Vig galena which gave an average on cube faces of 76.9. The Ivigtut galenas with less than 0.1 per cent silver gave 76.7 (No. 180 + 52) and 77.3 (No. 77).

Young & Millman (1964) for the Harz galena also give results on other orientations of the crystals and as mentioned earlier these results seem to indicate that a galena average VHN is close to the VHN of rhombododecahedral face. This again is close to the lowest value found on the cube face. This is also what has been observed in the present examination. It might therefore be valuable to set up the results of the measurements on the cube face from the series where the diagonals of the indenter were parallel with the cleavage.

In table 8 the differences between the maximum and the minimum VHN on the cube face have also been given. The average of this difference for all the Ivigtut galenas here treated is 11.7 and it varies between 8.6 and 14.6. There is no obvious correlation with silver content in this variation.

The minimum VHN from the cube faces of the Ivigtut galenas might also give an idea of the average VHN to be found on these galenas. Insofar as these values can be used in other deposits, from which oriented samples cannot be obtained, these values might represent a usable yardstick.

The variation in average-VHN with silver content when the silver dis-

Table 8. Average minimum VHN and difference between maximum and minimum VHN on the cube face of galenas.

locality	prep. no.	Min. VHN	Diff. VHN
Harz		69.0	8.5
Mesters Vig	85	73.3	7.2
Ivigtut	180	72.1	9.1
–	77	71.3	11.9
–	75	80.9	8.6
–	71	81.5	12.1
–	89	81.8	11.4
–	65	84.5	13.0
–	68	82.9	12.9
–	80	95.0	11.2
–	90	88.9	14.6
–	61	88.9	12.5

solved in the galena is connected with bismuth corresponding to the matildite molecule, is according to the presented material from 71 to 95 VHN corresponding to 24 VHN units. This is an increase of about 35 % in VHN for galena containing 5 % matildite compared to matildite-free galena.

Deformation of galena raised the average VHN of the galena from 82.75 to 98.45 corresponding to about 16 VHN or nearly 20 %, with a deformation amounting to 36 %.

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Dansk sammendrag

Vickers hårdheden, VHN_{100}, er blevet bestemt på orienterede spaltestykker af blyglans fra Ivigtut, Syd-Grønland, Mesters Vig, Øst-Grønland, samt på finkornet blyglans fra Bunker Hill, Idaho, U.S.A. Blyglansen fra Ivigtut indeholder op til 5 procent matildit i fast opløsning, hvorimod blyglansen fra Mesters Vig praktisk talt ikke indeholder fremmede stoffer. Blyglansen fra Bunker Hill var blevet underkastet forskellige grader af mekanisk deformation.

Stigende indhold af matildit og voksende Vickers hårdhed af blyglansen følges ad, hvilket tidligere, 1963, påvistes af Lebedeva. VHN-bestemmelser kan imidlertid ikke anvendes til bestemmelse af sølvindholdet, fordi indtrykshårdheden også afhænger af andre forhold.

Prøvens orientering og hårdhedsindtrykkets orientering viser variationer i blyglansens hårdhed på op til 20 VHN for den enkelte prøves vedkommende. Deformation bevirker stigende VHN; 36 procent sammentrykning fandtes at resultere i 20 procents stigning i VHN. Andre faktorer, det ikke er lykkedes at identificere i det foreliggende arbejde, synes også at indvirke på blyglans VHN.

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