

PRECISION LATTICE MEASUREMENTS OF GALENA

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ABSTRACT

Precision lattice determinations of galena are virtually lacking; this paper partly rectified this deficiency. The cube-edge for pure galena at 25° C. was found to be 5.9240 ± 0.0004 kX units. The process of pulverizing galena preparatory to x-ray examination causes crystal distortion which, however, is removed by gentle heating. The resultant sharp lines with very large Bragg angles enabled precision data to be obtained for the first time from x-ray powder photographs of galena. Such data made it clear that bismuth can substitute for lead causing a shrinkage of the unit cell.

Apparently identical galena specimens can readily be differentiated spectrochemically by means of their minor element content and to a lesser extent by the variation in their cube-edges. Some of the biggest differences were found in the galenas of the "Rand" gold mines. This information should prove useful to geologists in their investigations.

INTRODUCTION

The writer recently drew attention to the work of others which indicated that pyrite could conceivably assume the role sometimes of an "indicator fossil" (1); both duplication and differences in the values of the cube-edges of pyrite provided criteria. It was also stated there that other cubic minerals warranted attention; among them is galena. Fortunately, a collection of very small galena fragments was available from a previous, as yet unpublished, study of the minor elements in galena, as determined spectrographically. It was therefore decided to utilize some of these specimens in the determination of the cube-edge of galena; at the same time it was hoped to demonstrate that at least some of the minor elements did in fact occupy lead positions in the galena framework.

An added incentive was the thought that there was a possibility of recognizing the different geological origins of the samples by means of laboratory investigations of a modern kind. In this respect the work has probably not progressed sufficiently and a handicap is the lack of geological interpretation of the lead deposits. A start has, however, here-with been made and new data have been obtained that justifies publication at this stage. It is hoped hereby to interest geologists in a novel attack on their field problems. There is clearly a need for the accumulation of similar data on relatively common minerals, comparable to the work by Smith on pyrite (2). It is the writer's contention that modern laboratory methods are as yet not fully appreciated by field geologists in their academic as well as economic studies. In South Africa where

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geological correlation follows lithological lines, where particularly "gold reefs" are identified according to their disposition to certain "markers," varietal features of relatively common minerals deserve special study and take on a new significance.

PREVIOUS WORK

The new "Dana," volume I (3), quotes an averaged value for the cube-edge of galena which is derived from results of about 20 years ago, collected in the "Strukturbericht," viz:

$$a_0 = 5.93 \pm 0.02.$$

This result which has no pretensions to high accuracy is adopted also by Strunz in his "Mineralogische Tabellen" (4).

For PbS—no value for galena is listed—the well known "Handbook of Chemistry and Physics, 30th Edition" (5), gives the value 5.97.

In the A.S.T.M. set of x-ray diffraction cards, there is one precision result, obtained with Mo-radiation on a galena specimen whose origin is not given, viz:

$$a_0 = 5.9195 \text{ (Temp.?)}$$

The relative smallness of the "back-reflection" angles obtainable with Mo-radiation, added to the relatively high absorption of lead, would tend to give a rather low result in this instance, as comparison with the results in Table 1 would suggest. Of course, an impure specimen could also cause a lowering of the cube-edge—it is not known what precautions were adopted in this determination and this result is not acceptable as representing the true cube-edge of pure galena.

In any event one has to choose between this value and that given by von Zeipel (6) who selected his specimen with some care but failed to test it chemically in any way. He reports:

Galena, Příbram, at 18° C.

$$a_0 = 5.923_{34}$$

with the last two digits doubtful. This result is the only one that could be found in the literature which deserves serious consideration, and, as will be shown later, is correct as far as can be judged, to within the errors indicated, *i.e.*, to four significant figures.

Although all these results are reported in Ångströms, they are actually in kX units.

It is evident that there is need for reliable and accurate data on the lattice parameter of such a common mineral as galena. It is surprising to find that, despite the comparative simplicity of procuring such measurements on cubic minerals, there are probably no more than a half

dozen or so precision cube-edge determinations in the literature—apart from those on diamonds which have been the subject of more intensive investigations.

DISTORTION IN POWDERED GALENA

At the start of the investigation it seemed likely that at best a result with four significant figures could possibly be achieved if the conventional powder x -ray technique was to be used. Although the low θ values were indicated by sharp lines, the important large angle ones, *i.e.*, the back-reflections, were very diffuse. This is commonly encountered in minerals with a more complicated structure and in the so-called metamict

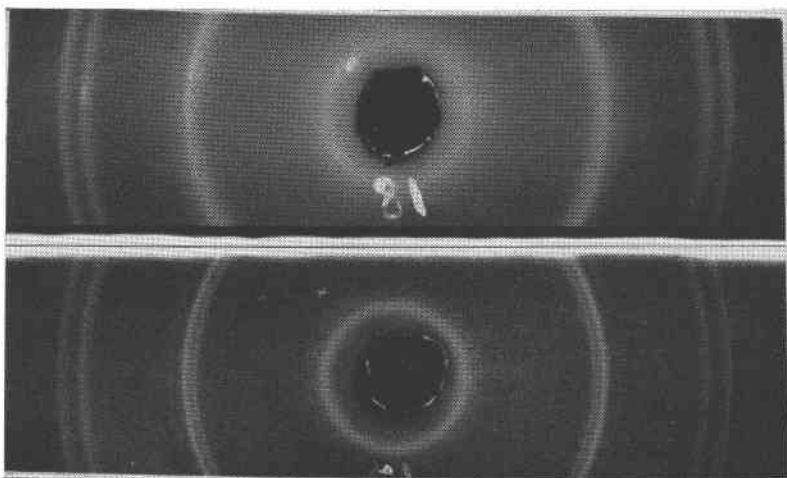


FIG. 1. *Top*: Back-reflection lines of galena before being heated.
Bottom: The same, after gentle heating.

minerals. The writer at first assumed the cause of this phenomenon to be inherent in the galena samples; it was thought to be largely due to small variations in composition coupled with zonal arrangement. When, however, the rather pure sample from Joplin, No. 1 in Table 1, also yielded fuzzy lines, it seemed possible that the cause lay in induced distortion or strain of the crystal structure as is found commonly in metals. Guided by metallurgical practice—the writer received much of his practical training in x -rays in the Metallurgical Department at M.I.T. under Professor T. J. Norton—and also with the knowledge that radioactive minerals yield better x -ray photographs after being heated, the powdered sample was heated to between 300 and 400° C. for a few minutes. The remarkable improvement in definition is apparent from Fig. 1 which shows the same sample before and after “annealing.”

It could readily be established that it was the grinding process which mainly, if not wholly, always caused the lattice distortion for, if the annealed powder was again ground, the sharp lines gave place to diffuse ones in the x -ray pattern. Although such phenomena are normally encountered in metals, they have apparently not been reported in minerals. It is of course known, even if not well known, that radioactive minerals also respond to annealing but they cannot then rapidly be made to revert to the previous strained condition. It seems likely that other minerals are affected by grinding in the same way as galena and would also respond to gentle heating to yield better defined x -ray powder patterns.

Discussing these observations in a letter to Professor Martin Buerger, the writer said. ". . . I found it was necessary to 'anneal' the powdered sample. . . . I take it that this is glide-translation phenomena for even around 200° C. the distortion is somewhat rectified. I am wondering whether relief of strain may also give sharper definition in single crystal work sometimes? . . . I do not think one has here the grain-growth as with your work on fluorite" (7). The writer is grateful to Prof. Buerger for the following comments in his reply: "Your remarks on galena are certainly interesting. The effect you have mentioned is a well-known one for plastic materials. When these are ground for powder samples they deform and this always results in lack of definition of the diffraction lines. This results from curved planes chiefly, and is an indication of the internal strain . . . it seems to me that I had read some place that when platinum is deformed it increases slightly in lattice constant. But I believe that the change is less than you have detected in galena. . . . Whether you recognize the effect as such or not, the decrease in fuzziness on annealing is equivalent to a recrystallization. I know that this annealing is customarily done to metallurgical powder samples to make the powder photographs readable. Incidentally, you can't do this to single crystals which have been bent and get a single crystal back. Instead you get an aggregate back. Furthermore you can't recrystallize a single crystal by annealing if it hasn't been deformed mechanically. Anyway, not in reasonable time. If one could, no single crystal would show lineage structure or other deviation from perfection if it had been grown at elevated temperatures."

APPARATUS AND METHOD

A Picker x -ray unit was used with unfiltered copper radiation. The x -ray tube was run at 35 KV and 20 MA, and exposures were usually for about 2 hours. The change of temperature of the camera during this period did not exceed 2° C. under operating conditions; the room in which the apparatus was housed was well ventilated. The temperature of the

sample was taken as the temperature of the camera, which was determined by placing a thermometer in contact with it; readings were taken at the beginning, during, and at the end of the exposure. The air temperature was also noted during this period. All the results were obtained in the narrow temperature range from 22° to 26° C. and these were corrected to correspond to a temperature of 25° C. Errors in temperature are considered to be less than one degree, which, in terms of the final cube-edge figure means that this source of error is less than 0.0001 kX units. Some crude insulation helped to reduce the heating of the camera due to the operation of the x -ray unit.

A Debye-Scherrer camera, as designed by Buerger (8), which had a diameter of 114 mm., was available. Kodak No-Screen x -ray film was used and, after processing, was allowed to dry and approach normalcy for a week before being measured. This was done by means of a commercial viewing box fitted with a fluorescent bulb, which did not create undue heat, and a measuring scale with vernier. By interpolation, measurements to a precision of 0.02 mm. could be duplicated. Films were at first measured twice using different parts of the scale but no added accuracy resulted nor were any real variations in results found.

The diffraction rings were measured on either side of the x -ray beam's exit and entrance holes; the determination of the centers of these holes on the scale gave two valuable check-points, one of which could be used for each pair of measurements. The difference between these two points enabled the "shrinkage correction" to be applied accurately and simply because of the Straumanis (9) method of film mounting in the camera used.

After the calculation of the cube-edge derived from the higher angles, the results were plotted graphically according to the method of Bradley and Jay (10) for the elimination of systematic errors, and the extrapolation gave the value for the cube-edge of that sample at the temperature at the time of determination. The correction which had to be added or subtracted from this value for each degree centigrade was taken as 0.000115 kX units;* the positive correction for refractivity for galena is 0.0001 kX units, calculated according to the method of Lipson and Wilson (11), and, in common with other workers, has been neglected.

The wave-length values used, were:

CuK α_1	1.537395 kX
CuK α_2	1.541232 kX
CuK β	1.38935 kX

The following seven points proved most useful in plotting the graph for

* The average of the slightly differing values of the coefficient of linear expansion for galena given in refs. 5 and 17 was used in this calculation.

the extrapolation to zero error, according to the method of Bradley and Jay, and are given in terms of $(h^2 + k^2 + l^2)$ and relevant copper radiation:

- (59) $K\alpha_1$
- (56) $K\alpha_1$
- (56) $K\alpha_2$
- (52) $K\alpha_1$
- (52) $K\alpha_2$
- (51) $K\alpha_1$
- (51) $K\alpha_2$

The point corresponding to (64) $K\beta$ was sometimes useful when its reflection was of sufficient intensity, for the precision in measuring was directly dependent on this factor. Points corresponding to (44) $K\alpha$ and (40) $K\alpha$ usually showed the straight line relation of the graph to change—often steeply—to a curve. These points because of the absence of resolution in the $K\alpha_1$, $K\alpha_2$ doublet, are not highly accurate and show the systematic errors due to eccentricity and absorption more markedly. Great care was taken in trying to place the small rods as centrally as possible; in order to counteract the effect of absorption these rod-like samples were kept as thin as was practicable viz. 0.2 mm. in diameter.

To ascertain with what accuracy the apparatus could operate with the technique employed, parallel determinations of the lattice constants of gold and silver were carried out. These serve as a basis of comparison in assessing the cube-edge determination of the galenas. Both metals were obtained from the South African Mint and were of exceptional purity; the gold had a fineness of 999.99 and the silver, 999.9. The procedures were exactly the same including the temperature observations.

There are slight differences in the published results of the lattice constants of the metals; those given in the new "Dana," Volume I, correspond to the values listed by Barrett (13), when reduced to the same temperature, and these have been used here in order to compare with the writer's determinations. The constants are given for 18° C. as:

	AS PUBLISHED	THIS WORK
Gold	4.0699 ± 0.0003 kX	4.0701 kX
Silver	4.0772 ± 0.0002 kX	4.0777 kX

This agreement is highly satisfactory and incidentally demonstrates with what accuracy Debye-Scherrer cameras with Straumanis film mounting can be used. Some published results of the lattice constant for silver suggest that the writer's value is perhaps not unduly high. In any event it is hardly beyond the combined limits of error, and the correction for temperature adds a slight uncertainty to the last digit. In such work it is reasonable to assume that the writer's error is comparable to those of other workers.

The diffraction patterns of the metals yielded somewhat sharper lines than those obtained with galenas. If this tended to increase the error, this effect must have been more than counteracted by the fact that galena yielded a higher Bragg angle. It must be exceptional that such a high angle, $85\frac{1}{2}^\circ$, could be utilized in the determination of a lattice constant.

The seven points plotted corresponded to angles from $85\frac{1}{2}^\circ$ to 68° for galena subjected to copper radiation. Taking into consideration factors of thermal expansion, x-ray absorption, elimination of strain, line sharpness and the like, it seems reasonable to assess these as not too different in respect of accuracy between the metals and galena as to increase the over-all limits of error unduly. It is believed that this can be safely taken as 0.0004 kX and probably, in most determinations, as less. The cube-edge results of galena are given in this paper subject to this limit of error, viz. ± 0.0004 kX and therefore may be regarded as precision determinations.

SPECTROGRAPHIC EXAMINATION

Small cleavage fragments of selected material—often from polished, ore-sections which had previously been checked for homogeneity under the microscope—were placed on flat copper electrodes which were made the cathode, and arced for 20 seconds at 5 amps. before a large Hilger Littrow type spectrograph set for the range 2800 to 5000 Å.

To assess roughly the amounts of the more important minor components, lead sulfide was precipitated which contained 1% respectively of the metals Bi, Sb, Cd, and Sn, also in the form of sulfides. This precipitate was diluted with pure lead sulfide to give the lower concentrations. These mixtures served as standards in determining the order of magnitude of the four elements present in individual galena samples, by comparing visually the intensities of element lines in the spectra. The quantitative results listed in Table 1 should not be interpreted too rigidly. A number of other elements were found—some of these appear in Table 2—but either they could not be used diagnostically or they were conceivably derived from contaminants. Here the role of silver could not be assessed and its great sensitivity in the spectrographic examination did not allow the estimation of even very approximate amounts in the samples. It did allow the detection of the extremely small amounts of silver in the Joplin sample. Very small amounts of thallium were frequently found, usually at the threshold sensitivity of the method used and special refinements of technique would be necessary to obtain quantitative information.

The spectrographic method used here, as stated earlier, was never intended for this particular study; as always it represents a compromise. It is considered adequate for the present purpose and enabled the selec-

tion of suitable material for the determination of the cube-edge. There was not much difficulty in duplicating results; different samples from the same locality showed very little variation in results—a factor, which is relevant in comparing von Zeipel's determination (6) on the galena from Příbram, Bohemia, with that of the writer's. This is discussed below.

The value of linking spectrographic tests with *x*-ray work deserves emphasis and certainly helps to complete the picture—especially in the absence of any chemical examination. Such tests however are not exhaustive; for example, they would not indicate a sulfur deficiency in the galenas.

RESULTS

The tabulated findings in Table 1 briefly summarize the results of the present investigation; the arrangement is such as to show some of the influences of geological origin and locale. Eight South African specimens were selected as the spectrographic work dealt primarily with local ores; the two overseas samples were included, as one, Joplin (No. 1), is the purest, while the other from Příbram, No. 3, was examined in order that

TABLE 1. SPECTROGRAPHIC AND X-RAY RESULTS ON GALENA

Sample No.	Locality: Farm or mine	Geological Environment	Sn	Sb (Per cent)	Cd	Bi	a_0 @25° C. (kX units)	
(1)	Joplin area	Replacement of flat-lying Limestones.	0	0	0	0	5.9240	
(2)	Bokkraal 300, W. Transvaal	Replacement of flat-lying Limestones.	Tr	0.1	0.02	Tr	5.9232	
(3)	Příbram, Bohemia	Quartz } Veins } (in Diabase) (in Jaspers)	Tr	0.1	0	0	5.9236	
(4)	Langlaagte, 1693 N. Transvaal		(in Granite)	0	0	0.01	0.01	5.9230
(5)	Union Lead and Silver Mine, Pretoria Distr.		(in Diabase)	0	0.02	Tr	0	5.9233
(6)	Balloch, 0.136, N.W. Cape Province		(in Jaspers)	Tr	0.05	0.05	Tr	5.9235
(7)	Zaaiplaats Tin Mine, Transvaal		Late hydrothermal accessory in "tin pipes" of the Bushveld Granite	Tr	0.1	0.01	0.01	5.9240
(8)	City Deep Gold Mine, Johannesburg	Minor accessory in the auriferous conglomerates of the Witwatersrand System	0	0.05	Tr	0	5.9235	
(9)	C.M.R. Gold Mine, West Rand.		Tr	0.02	.02	1.0	5.9223	
(10)	New Modderfontein Gold Mine, Benoni		0.02	0.1	Tr	>1.0	5.9190	

its result could be compared with the work done by von Zeipel on a similar specimen.

The geological grouping throws little light on the results and this may be attributed to the fact that galena forms over a wide range of temperature and conditions as may be learnt from the recent "Symposium on the Geology, Paragenesis, and Reserves of the Ores of Lead and Zinc" of the last International Geological Congress held in London (1948). Too few results are presented to cover this aspect, but among the groups, it appears, that locality exercises an influence: Galenas of the same origin tend to differ rather than to agree in minor element content and the concept of mineral provinces finds support. It is clear how readily galenas from different localities can be differentiated—although apparently identical even after microscopic examination. The results on the galenas from the South African gold mines, Nos. 8–10, indicate how unfortunate it is that galena is a relatively rare constituent of the auriferous conglomerates of the Witwatersrand system, as the mineral here shows promising possibilities to serve as an indicator in "reef" correlation problems.

The frequency with which certain elements occur in 60 galena specimens tested spectrochemically is given in Table 2; it must be noted that the sensitivity of detection for the different elements is not the same. However, spectrographic sensitivity is not a controlling factor for the order of the elements in the table; elements that were less frequently detected are by no means those of poorer sensitivity. An interesting by-product of this investigation was the conclusion that vanadium, despite certain opinions to the contrary, hardly if ever is found in galena (14); the limit of detection for this element was less than 0.005% V_2O_5 .

TABLE 2. FREQUENCY OF OCCURRENCE OF MINOR ELEMENTS IN 60 GALENA SAMPLES

Ag.....	100%
Sb.....	80%
Cd.....	70%
Bi.....	50%
Sn.....	40%
Fe.....	40%
Tl.....	35%
Mn.....	30%
Sr.....	20%
V.....	tr?

Apart from silver, the four elements listed in Table 1, viz. Bi, Sb, Cd, and Sn, are the only ones that occur in "chemical amounts" in galena, and only bismuth in possibly major amounts. Only this element occurs in sufficient quantity to affect noticeably the cube-edge value, while such elements as Sr, Tl, Fe, and Mn probably never exceeded 0.01% in any

galena sample. No sympathetic or antipathetic relationship of the minor elements could be observed.

TABLE 3. IONIC RADII OF ELEMENTS (VARIOUS AUTHORITIES)

Pb ⁺²	Ag ⁺¹	Bi ⁺³	Bi ⁺⁵	Sb ⁺³	Sb ⁺⁵	Sn ⁺²	Cd ⁺²	Sr ⁺²	Tl ⁺³
1.18— 1.32	1.13— 1.26	1.20	0.74	0.90?	0.62	1.02	0.97— 1.3	1.13— 1.27	0.95— 1.05

Table 3 lists the ionic radii which, of course, can vary with coordination and are not too accurately known. Nevertheless, it is clear that the size of the ions is in keeping with the common substitutions found; such elements as manganese and iron are too small for substitution and the extreme minuteness of the amounts found are best explained by contamination, especially when one considers the frequency, in this country, of the association of lead deposits and wad.

There is no difficulty in correlating size of ion with isomorphous replacement of Pb⁺² by Ag⁺¹, or Bi⁺³, or even such unusual elements as Tl⁺³ and Sr⁺², in galena. The chalcophile nature of lead is in conflict with the lithophile one of strontium, and this precludes any high degree of isomorphism in nature despite the close similarities of the two ions. Cd⁺² and Sn⁺² fall just within the 15% limit of tolerance for size suggested by V. M. Goldschmidt and it is, therefore, not surprising to find that they also only occur in very limited amounts in galenas.

The fact that antimony occurred so frequently in local galenas—and then in “chemical amounts”—suggests that the rather doubtful size of Sb⁺³ has been taken at too low a value. This explanation is suggested because of the relative rarity of the antimony-bearing minerals, boulangerite and tetrahedrite, in South African lead deposits (15). Most of the galenas were tested under the ore microscope for homogeneity; tetrahedrite would have revealed itself by its common accessory elements, such as zinc and arsenic, during the spectrochemical examination. Galenas showing the presence of zinc, of which there were very few, were discarded as the zinc was due to contaminating sphalerite: this also could be deduced from the increase in such elements as cadmium, iron, indium, etc. It is, therefore, concluded that Sb⁺³ can substitute fairly readily for the metal in galena. There is thus a certain uniformity in behavior of the similar elements bismuth and antimony: their analogues of galena are bismuthinite and stibnite, and here the metals are trivalent. It is the trivalent ion that can replace Pb⁺² because of the size relationship between the ions; the higher charge is also a favorable factor in aiding such replacement.

There is an alternative consideration in explaining the introduction

of cadmium, which may operate with other elements also. One has to consider that there are two known forms of CdS: one is greenockite which has the crystal structure of wurtzite; the other is CdS (β), which has the same cubic structure as the commonest associate of galena, viz. sphalerite. It is true that its cubic structure differs from the one of galena but the parameters are very close: 5.92 and 5.82. The unit cell in each case contains four formula weights. Miscibility between these compounds is a likely explanation of the presence of cadmium in galena. In contrast, argentite could not conceivably enter such substitution as its cube-edge differs markedly, viz. 4.88. A zonal distribution of silver in some galena specimens has been reported (16). As the role of silver in galenas will be tested by synthesis, the question is not further elaborated here.

The replacement of lead by bismuth in galena has been commonly accepted; it has probably never been so clearly demonstrated as here, in the cube-edge variations that result from this element entering the galena lattice. In Table 1 the cube-edge results show a remarkable uniformity from Nos. 1 to 8: the variations hardly exceed the maximum limits of errors that have been assumed. On the other hand, the only samples that contain a foreign element in appreciable amounts, Nos. 9 and 10, are characterized by a marked and progressive reduction of the unit cell, corresponding to the amount of bismuth found in the samples. Both Wahlstrom (17) and Oftedal (18) have reported the presence of bismuth up to about 2% in galenas and have discussed the effect of this element on octahedral cleavage and parting in such galenas.

The ionic radii involved suggest that a shrinkage could have been predicted by a replacement of Pb^{+2} by Bi^{+3} . In the absence of any evidence that galena, like pyrite, may sometimes have a deficiency of sulfur, it must be concluded when weighing the results obtained on galenas from ten different localities, that isomorphic substitution does in fact take place as suggested and that substitution causes the unit cell to become measurably smaller.

The way is now opened to synthesize galenas and substitute bismuth in the lattice in increasing amounts and measure the resultant shrinkage of the cube-edge; such findings may find application in the field investigations of lead silver deposits.

In determining the parameter for galena one could take the average of the values from samples No. 1 to No. 8 and this is 5.9235 kX. In view of the fact that No. 1, *i.e.*, the sample from Joplin, was the purest galena examined here, it is proposed to take its value, as representative of pure natural galena until such time as a purer specimen is measured:

Galena, Joplin, Mo., at 25° C.

$$a_0 = 5.9240 \pm 0.0004 \text{ kX}$$

Actually this value is the result of a duplicate determination: when doing the first, the temperature was not noted but it can be assumed to lie, with the other determinations, in the range of 22° to 26° C. The first determination gave the result of 5.9239 kX—which, despite a small possible error, demonstrates with what precision results can be duplicated.

It became interesting to compare the proposed value for the cube-edge of galena with that determined by von Zeipel (6), mentioned earlier. At the same time it was desirable to work on a similar specimen to the one examined by him. A number of different specimens of galena from Příbram, Bohemia, were obtained from museum collections and subjected to spectrographic examination for minor elements. They all gave rather similar results and one of these, No. 3, in Table 1, was used for a cube-edge determination. The following results, neglecting errors, show a very satisfactory agreement:

Galena, Příbram, at 25° C.

$a_0 = 5.9241$ kX.....	von Zeipel, 1936 (6)
$a_0 = 5.9236$ kX.....	This work, 1950

These results by two different workers using different methods certainly support the proposed cube-edge value of galena.

The determination with precision of the galena parameter now allows a check of the “*d*-spacings” given in the A.S.T.M. *x*-ray cards; Table 4

TABLE 4

Calculated, $a_0 = 5.9240$ kX	A.S.T.M. Card II—1452	A.S.T.M. Card II—3992
3.500	3.42	3.42
2.962	2.96	2.960
2.095	2.08	2.093
1.786	1.785	1.785
1.710	1.710	1.709
1.481	1.480	1.480
1.359	1.360	1.358
1.325	1.325	1.324
1.2093	1.220	1.2083
1.1401	1.140	1.1392
1.0472	1.049	1.0464
1.0014	1.004	1.0006
0.9874	0.989	0.9866
0.9367	0.938	0.9360
0.9034	0.905	0.9027

shows the fairly good agreement obtained between the calculated and observed spacings recorded on two of the cards.

SUMMARY

(1) The crystal distortion resulting from the process of grinding galena intended for powder x -ray work, can be removed by gentle heating of the ground powder.

(2) The resultant sharply defined pattern with exceptionally high Bragg angles for copper radiation enabled precision cube-edge determinations of galena to be made on samples of various origins and of differing purity.

(3) The purest galena found after spectrochemical analysis gives the following result which is suggested as the best known value for this parameter:

$$\begin{aligned} & \text{Galena, Joplin, Mo., at } 25^\circ \text{ C.} \\ & a_0 = 5.9240 \pm 0.0004 \text{ kX} \end{aligned}$$

(4) Apart from the ubiquitous silver, the common minor constituents of galena, in "chemical amounts" are antimony, bismuth, cadmium and tin. Their substitution for lead is discussed briefly, chiefly from the viewpoint of similar ionic radii.

(5) Only bismuth was found to substitute for lead to any appreciable extent in galena; the effect was to lower the value of the cube-edge so that differences were easily measurable.

(6) Apparently similar specimens of galena show diagnostic differences but these cannot at present be correlated with geological origin; the spectrograph rather than the x -ray unit discovers these differences readily.

(7) Among galenas of similar origin the minor element content tends to support the concept of "mineral provinces."

(8) The calculated " d -spacings" are compared with the data furnished by the A.S.T.M. x -ray cards.

(9) This laboratory approach to geological field problems is considered worthy of the attention of both academic and economic geologists.

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The writer was introduced to x -ray work while at M.I.T. as guest visitor during the period 1946-1947; certain facilities were provided by the Mineralogical Department at Harvard, also. It is with pleasure that the writer records his indebtedness to the authorities and teachers who so generously provided a foreigner an opportunity to study in the U.S.A.

Several colleagues of the U. S. Geological Survey, Messrs. Christ,

Murata, and Fleischer, sought useful references and read through the writer's manuscript critically—these labors are gratefully acknowledged.

The work was done almost wholly in the laboratories of Mines Department in Pretoria and Johannesburg; here the writer wishes to thank Mr. Hardy for the use of equipment.

REFERENCES

1. WASSERSTEIN, B., *Am. Mineral.*, **34**, 731 (1949).
2. SMITH, F. G., *Am. Mineral.*, **27**, 1 (1942).
3. DANA'S System of Mineralogy, 7th Ed., Vol. **1**, pp. 201, 204 (1944).
4. STRUNTZ, HUGO, *Mineralogische Tabellen*, 2nd Ed. (1949); Akad. Verlag Gesellschaft, Giest u. Portig, p. 79.
5. *Handbook of Chemistry and Physics*, 30th Ed. (1947), p. 2040; Chemical Rubber Publishing Co.
6. VON ZEIPEL, E., *Arkiv. Mat. Astron. Fys.*, **25**, (1936).
7. BUERGER, M. J., *Am. Mineral.*, **32**, 296 (1947).
8. BUERGER, M. J., *J. Applied Physics*, **16**, 501 (1945).
9. STRAUMANIS, M. E., *J. Applied Physics*, **20**, 726 (1949).
10. BRADLEY, A. J., AND JAY, A. H., *Proc. Phys. Soc.*, **44**, 563 (1932).
11. LIPSON, H., AND WILSON, A. J. C., *J. Sci. Instruments*, **18**, 146 (1941).
12. *Handbook of Physical Constants*, *Geological Soc. Am.*; *Special Papers* #36
13. BARRETT, C. S., *Structure of Metals*, McGraw-Hill (1943).
14. WASSERSTEIN, B., *Proc. Geol. Soc. S. Africa* (1945), p. 1, xxxii.
15. WILLEMSE, J., SCHWELLNUS, C. M., BRANDT, J. W., RUSSELL, H. D., AND VAN ROOYEN, D. P., *Union S. Africa Dept. Mines, Geol. Survey, Memoir* **39** (1944).
16. FRONDEL, C., NEWHOUSE, W. H., AND JARRELL, R. F., *Am. Mineral.*, **27**, 726 (1942).
17. WAHLSTROM, E. E., *Am. Mineral.*, **22**, 906 (1937).
18. OFTEDAL, I., *Norsk Geol. Tids.*, **22**, 61-68 (1942).

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