OBSERVATIONS ON TWO PRECISION LATTICE MEASUREMENTS OF PYRITE FROM LEADVILLE, COLORADO

B. Wasserstein, *Geological Survey, Union of South Africa.*

ABSTRACT

Two recent, independent determinations of the cube-edge of pyrite from the same locality gave rather divergent results. A study of the two papers indicated that the differences are apparent rather than real—in fact, the results are in remarkable agreement with each other. It is thought that such agreement in the light of known variations in the properties of pyrite may be of some significance to the geologist.

INTRODUCTION

Precision lattice determinations of minerals are not yet common and not always practicable. Generally, results of high accuracy may be thought to serve no particular purpose but for certain mineralogical problems, and possibly some geological ones, precision data become desirable. The minerals of the cubic system whose paramaters can so readily be determined by x-ray powder methods with great accuracy, deserve greater attention in this respect. Among these minerals there are a number which by virtue of their significance in ore deposits, attract attention, e.g. pyrite; gold; galena; chromite; magnetite; uraninite, etc.

It was disconcerting, however, to find that on separate samples of pyrite from the same locality, the following results have been published by two prominent teams of mineralogists:

PYRITE, LEADVILLE, COLORADO

$a_0 = 5.4079 \pm 0.0005$Å......................................Peacock and Smith (1941)
$a_0 = 5.40667 \pm 0.00007$Å...........................Kerr, Holmes and Knox (1945)

Data of the accuracy claimed here are almost totally lacking for minerals; Kerr et al. do not try to explain the difference in the two cube-edge measurements and the object of this paper is to try to reconcile these results if possible.

CHEMICAL ASPECTS

Small variations in the composition of pyrite are known to exist and it has been shown that such differences affect the value of the unit cell (Peacock and Smith; Bannister and Hey, etc.). Peacock and Smith selected their Leadville sample because it approached perfection both physically and chemically; while the Kerr team tacitly assumed such perfection as their result is used to typify pyrite.

In the absence of any other possibilities of errors, both results of the

Leadville pyrites could be accepted as correct on the basis that the sample examined by Kerr and co-workers was chemically imperfect: a deficiency of sulphur in their specimen could readily account for the lower result. Smith (*Am. Mineral,* **27,** p. 9) records that ". . . pyrite may vary from $FeS_{2.00}$ to $FeS_{1.94}$ and still contain essentially nothing but iron and sulphur."

A corollary of importance would be that there are at least two distinct types of pyrite at Leadville.

TEMPERATURE CONSIDERATIONS

In neither paper are temperature effects considered. Reliable linear coefficients of thermal expansion of minerals are difficult to find; the best value is probably given in the *G.S.A.* publication "Handbook of Physical Constants" (Special papers No. **36**). One arrives at a value of nearly 0.00005 Å per degree centigrade in the variation of the cube-edge of pyrite. The degree of accuracy claimed by Kerr et al., viz. 0.00007 Å, becomes obviously untenable for it would mean that a variation of only $1\frac{1}{2}°$ C. would exceed the limits of total error admitted. Very special temperature safeguards over the period of radiation would be necessary in order to obtain the accuracy claimed and from such considerations one must conclude that the Kerr value cannot possibly exceed five significant figures, and at best can be given as:

$$a_0 = 5.4067 \pm 0.0001 \text{ Å}.$$

A "room temperature" difference of at least 12° C. would therefore fully account for the divergence in results if the limits of errors in both values are fully extended. It is, however, more likely that about 25° C. have to be assumed to represent the difference in temperatures in the two laboratories and this is hardly likely even when taking the heating effect of the x-ray units into account.

The effect of temperature certainly cannot be neglected and constitutes an important source of error in precision work of minerals with a relatively high co-efficient of expansion. It is improbable that temperature alone could explain the two divergent values.

WAVELENGTHS

Peacock and Smith state the wavelengths used by them, and these are the corrected Siegbahn units, i.e. Ångstroms; but they are not consistent in this usage as for their calibration they use the "Strukturbericht" value of the cube-edge for copper which although given in Ångstroms, is really in kX-units.

Kerr and his colleagues do not mention what wavelength value was

used but give their results in Ångstroms. There are sufficient data to check this and it is found that kX-units have in fact been used: their result is therefore not directly comparable with the Peacock-Smith figure as given.

It is relevant here to quote from a letter to "Nature" (VI, 151, p. 502, 1943) written by Lipson and Riley of the Cavendish Laboratory, which deals with this sort of looseness in the expression of x-ray units: " . . . it has been the custom to quote all results as though they were in Ångstrom units. . . . May we suggest the adoption of the following conventions? When an accuracy not better than 0.1% is claimed, the result should be given in Angstrom units, but for higher accuracy . . . in X units. The lattice parameter for iron could be given as 2.86 Å or 2860.4 X units, but not as 2.8604 Å. The wavelength adopted should always be explicitly stated. . . . "

These are sound conventions which are appreciated after examining the two papers under discussion.

Bearing in mind the remarks made in respect of temperature correction, the cube-edge for the pyrite sample from Leadville given in the paper by Kerr et al. becomes:

$$5406.7 \pm 0.1 \text{ X-units.}$$

Had Peacock and Smith given their result for the Leadville sample in X-units, the value would have been:

$$5407.0 \pm 0.5 \text{ X-units.}$$

Within the limits of error the two results obtained by independent teams of workers are now found to be in very good agreement.

SYSTEMATIC ERRORS

Every experimental method is subject to certain inherent errors and it remains to consider this aspect in the two determinations. In equipment and in the method of elimination of systematic errors, Kerr and his colleagues have closely followed Jette and Foote whose lattice determinations are considered amongst the best available.

The corrections applied by Peacock and Smith after a single calibration using pure copper as a standard, and with a confusion in wave-lengths, in respect of the cube-edge value for copper, invite criticism. The correction graph based on copper requires a slight extension in a straight line to cope with the higher angles of pyrite.

In order to test out this empirical type of correction graph evolved by Peacock and Smith, the writer prepared similar graphs using highly purified gold and silver as standards, a similar camera but different radia-

tion, viz. copper. A rough parallelism could be noted between the three graphs but the corrections appeared to be a function of the standardizing substance used.

As the well established extrapolation technique worked out by Bradley and Jay (*Proc. Phys. Soc.*, **44**, p. 563, 1932), is more accurate, rapid and convenient, there is nothing to be gained by the method employed by Peacock and Smith. From their data it is possible to ascertain the glancing angles they must have actually measured on their film; using these—a very small error may have been introduced in taking readings off the reconstructed correction graph—and the following wavelengths:

$$Fe-K_1 = 1932.076 \text{ XU}$$
$$Fe-K_2 = 1936.012 \text{ XU},$$

the cube-edge of pyrite for the three (hkl) values were plotted against $\cos^2 \theta$ and extrapolated to zero error. This gave the final value, with the plotted points falling on a good straight line, as:

$$a_0 = 5406.6 \text{XU}.$$

This result is considered to be nearer the true value than the one obtained by converting the Peacock-Smith figure into X units.

The limits of error have not been accurately assessed, but are considered to be now much less than assumed by Peacock and Smith. Based on the experience of the writer, this error will probably not exceed 0.3 XU; or dividing by a thousand, 0.0003 KXU.

Conclusions

The findings of the two papers may now be summarized in this way: Pyrite, FeS_2, Leadville, Colo., at "Room Temperature".

$a_0 = 5.4066 \pm 0.0003$ KXU.............................Peacock and Smith (1941).
$a_0 = 5.4067 \pm 0.0001$ KXU...........................Kerr, Holmes, and Knox (1945)

These determinations show a truly remarkable agreement and one is inclined to assume that, therefore, the two samples were chemically identical and that the temperatures at the times of exposure were probably very similar.

Peacock and Smith show that the introduction of nickel, which is a well known "contaminant" of pyrite, appreciably raises the length of the cube-edge while a deficiency of sulphur somewhat lowers the value. This latter phenomenon is shown by the other measurements of a pyrite given in their paper, which when re-determined and extrapolated to zero error as with the Leadville sample, gives the following result:

Pyrite, $Fe_{1.98} \pm 0.01$, Elba, at "Room Temperature"
$$a_0 = 5.4050 \pm 0.0003 \text{ KXU}$$

The pyrites from the two widely separated localities are therefore clearly different and this difference is readily measurable and recognizable by a comparatively simple x-ray technique.

Peacock and Smith have shown the high accuracy obtainable with a Debye-Scherer camera using the Straumanis method of film mounting. If to this is added the graphical method of Bradley and Jay for the elimination of systematic errors—and perhaps, the correction for refractivity, which is usually neglected—cube-edges can be determined with the highest precision. The difficulty of overcoming temperature effects may well prove a barrier to increased accuracy with focusing types of cameras—especially where the samples possess relatively high coefficients of expansion, and require lengthy exposures.

There is clearly a need for further accurate data on the Leadville pyrite which because of its apparent perfection could become a "standard." Pyrite is very common, and is associated with economic mineral occurrences of diverse kinds. From the work of Smith it is known that there are large variations in the properties of pyrite. It would be very useful to the geologist if he could differentiate between various pyrites with ease and certainty, and this seems quite feasible by powder x-ray diffraction, preferably linked with spectrographic data. Such an approach allows one to work with minute quantities and to obtain quantitative results which facilitate correlation. It is reasonable to assume that somewhere the mineral pyrite may well prove as useful as an "indicator fossil"—it remains to collect the relevant data.

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