Acta Cryst. (1956). 9, 169

The Elasticity of Iron Pyrites, FeS_2

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(*Received* 25 *July* 1955)

The elastic constants of iron pyrites, FeS_2, have been determined by a photographic method. The diffuse reflexion associated with the reciprocal-lattice point 440 was studied, using Mo $K\alpha$ radiation and a zirconium screen in front of the photographic film. Two photographs were obtained with the [001] axis inclined to the vertical at 0° and 45° respectively. A microdensitometer survey of the diffuse spots enabled the elastic ratios c_{12}/c_{11} and c_{44}/c_{11} to be determined. These were combined with the known value of the cubic compressibility to give the values

$$c_{11} = 37\cdot(7),\ c_{12} = 3\cdot(2),\ c_{44} = 10\cdot(9) \times 10^{11}\ \text{dyne cm.}^{-2};$$
$$s_{11} = 2\cdot6(9),\ s_{12} = -0\cdot002,\ s_{44} = 9\cdot(2) \times 10^{-13}\ \text{cm.}^2\ \text{dyne}^{-1}\ .$$

Contrary to the findings of previous investigators, c_{12} is positive and s_{12} is negative. Thus the only previously accepted exception to the rule that s_{12} is of opposite sign to s_{11} appears not to be an exception.

Introduction

The elastic properties of iron pyrites have long presented several problems. Voigt (1910) gave values which showed that in magnitude the elastic constant c_{11} of this crystal was higher than for any other known substance. Since then tungsten (Schmid & Boas, 1935), diamond (Bhagavantam & Bhimasenachar, 1946) and corundum (Bhimasenachar, 1950) have been shown to have higher values of c_{11}, but still it is remarkable that iron pyrites should have so large an elastic constant.

A second noteworthy character was the negative value of c_{12} and the corresponding positive value of s_{12}. The meaning of a positive value of s_{12} can be expressed as follows. If in the direction of a side of the unit cell a stretching force is applied, then in a direction perpendicular to this cell edge an expansion will occur if s_{12} is positive. Naturally this is the opposite of what usually happens. Voigt (1910) also found a positive value for s_{12} in $NaClO_3$ (which was subsequently found incorrect), but apart from this no other reported observation of such a positive value exists. Bhagavantam & Bhimasenachar (1944) and also Doraiswami (1947) reinvestigated the elastic properties of iron pyrites, using the supersonic waves method, and obtained values substantially in agreement with Voigt, including the positive value of s_{12}.

Because of the high numerical value of the elastic constants c_{11} and c_{44}, iron pyrites scatters relatively little diffuse X-rays. More than usual care must therefore be devoted to obtaining adequate measurements. The fluorescent K radiation from the iron atoms is the principal difficulty. However, these difficulties were largely overcome in the work described below.

A thorough study of iron pyrites would include an investigation of crystals of composition varying over the known range ($FeS_{1.94}$–$FeS_{2.01}$) (Smith, 1942). The structure may be defective in sulphur atoms or in iron atoms relative to the stoichiometric composition. The present crystal was found to be thermoelectrically negative relative to copper, and to have a low specific resistance and a positive temperature gradient of resistance. Smith (1942) found such an association of physical properties was associated with a structure defective in sulphur atoms. The chemical composition of this crystal was kindly determined by Mr J. H. Scoon of the Department of Mineralogy and Petrology and found, however, to be $Fe_{0.981}S_{1.971}$.

Experimental method

A crystal of iron pyrites, showing the common {210}, {100} combination of forms, was cut parallel to the (110) face. After cutting, this face was lightly ground and finally etched with concentrated nitric acid. A portion of the face, free from holes or other obvious inhomogeneities, was selected for study. The crystal was set up on a Unicam oscillation goniometer with the (110) plane inclined at an angle to the collimator just less than the Bragg angle. After preliminary experiments with Co radiation, the fluorescent background was avoided by using Mo $K\alpha$ radiation and a zirconium sheet, 0·0045 in. thick, attached to the black paper which enclosed the film. The camera radius was 5·73 cm. The following data apply to this experiment:

Cell side $a_0 = 5\cdot41$ Å; θ (Bragg) $= 21° 50'$; angle of incidence, $i = 20° 10'$; $\lambda = 0\cdot71$ Å; $s = 0\cdot020$ (nomenclature is the same as that given by Hoerni & Wooster (1952)).

Two photographs were taken: in the one, called 'symmetrical', the [001] axis was parallel to the goniometer axis, i.e. vertical; in the other, called 'inclined', the (110) face of the crystal was rotated in its own plane through 45°. In taking the 'inclined' photograph, the upward-pointing end of the [001] axis was directed away from the photographic film.

The intensity distribution over the diffuse spot was measured in an automatic recording microdensitometer (Wooster, 1955). The blackening was measured along lines 0·5 mm. apart covering the whole spot. The objective and aperture in front of the photo cell were chosen so that the area of the film from which light was reaching the photo cell was $\frac{1}{6}\times\frac{1}{6}$ mm. The zirconium sheet did not absorb the radiation quite uniformly, and fluctuations occurred in the pen trace greater than is usual with diffuse X-ray photographs. However, a smooth line could be drawn through them and from this line the readings were made. These readings were plotted on a scale such that 1 mm. on the film corresponded to 24 mm. on the plotted diagram. The background at the sides of the area was subtracted from the readings, allowance being made for small variations of background from one side of the spot to the other. The 'skew' correction (Ramachandran & Wooster, 1951) was applied to correct for the fact that the angle of reflexion varies over the spot.

The coordinates of the diffuse spot were related to the position on the film of the Laue spot and the corresponding Bragg spot. For this purpose a separate photograph was taken in which the Bragg spot was produced at about the same density as the diffuse spot in the previous photograph. The size of this Bragg spot was used in applying a divergence correction. The distances of the diffuse spot and the corresponding Bragg spot from the central hole punched in the film were measured on the microdensitometer, and this afforded a check on the value of the angle of missetting from the Bragg position. This angle was, however, more accurately determined in setting up the crystal. A Geiger counter operating a ratemeter was used to determine the Bragg setting and the reading was then taken on the goniometer divided circle. The crystal was rotated through 1° 40′ from this setting so that the value of s should be 0·02. Charts for this value of s have been produced and greatly facilitate the interpretation (Hoerni & Wooster, 1952).

The centre of the 'symmetrical' diffuse spot can readily be found because of the line of symmetry passing through it. It is more difficult, from the coordinates alone, to determine the centre of the 'inclined' diffuse spot, and this was finally done by reference to the calculated contours of the diffuse spot. The calculated contours were fitted as closely as possible to the observed contours and the centre of the calculated contours was then taken to be the centre of the observed spot. The full curves in Fig. 1 give the contours of the experimentally determined densities for 0·7, 0·5 and 0·3 of the density at the centre of the diffuse spot.

Interpretation of the density distribution

By graphical construction, using the $\bar{\varrho}, \bar{\varphi}$ chart (Hoerni & Wooster, 1952), the positions on the contoured diagram of certain rekhas are marked in. On Fig. 1(*a*) [010], $[\bar{1}10]$, $[\bar{1}11]$ and $[\bar{1}1\bar{1}]$ are shown and on Fig. 1(*b*) [010], [001], $[\bar{1}11]$ and $[\bar{1}10]$ are given. Although individual points are subject to considerable errors it is useful to relate these particular points to the corresponding elastic constants. The distance, R, of the relp 440 from the Ewald sphere along each rekha was determined graphically and expressed as a ratio involving R_0, the shortest distance between the relp and the reflecting sphere. These ratios, $(R_0/R)^2$,

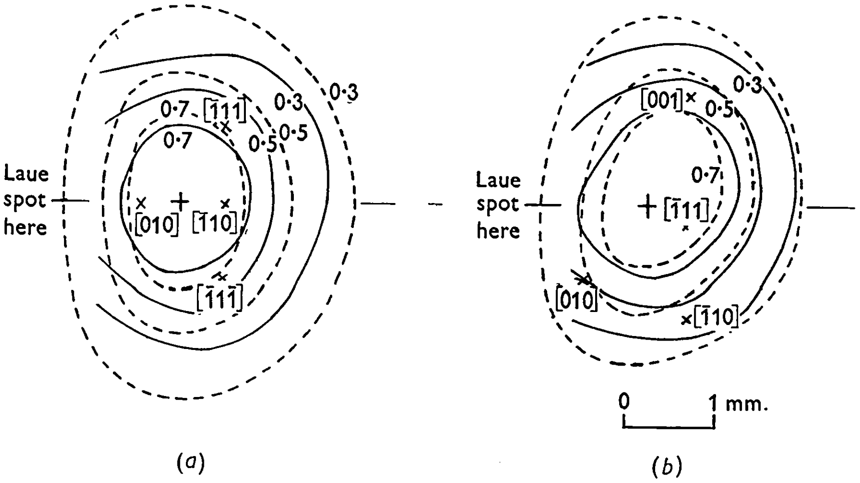

Fig. 1. (*a*) Microdensitometer plot for the 'symmetrical' photograph obtained with the 440 reflexion. The full lines are observed contours of equal density. The three lines correspond to 0·7, 0·5, 0·3 of the density at the centre of the diagram. The broken lines are the calculated contours, using the present values of the elastic constants.

(*b*) Similar diagram, but applied to the 'inclined' photograph.

Table 1

Photo	Relp $[ABC]$	Observed intensity, I	$\left(\frac{R_0}{R}\right)^2$	$I\left(\frac{R}{R_0}\right)^2$	$K[ABC]_{440}\times c_{11}$
Symmetrical	$[010]$	29	0·85	34	$\frac{1}{2}(1+1/\chi_{44})$
	$[\bar{1}10]$	29·5	0·83	35·5	$2/(1-\chi_{12})$
	$[\bar{1}11]$	21·5	0·57	37·5	$3/(1-\chi_{12}+\chi_{44})$
	$[\bar{1}1\bar{1}]$	21	—	—	—
Inclined	$[010]$	25	0·54	46·5	$\frac{1}{2}(1+1/\chi_{44})$
	$[001]$	31	0·43	72	$1/\chi_{44}$
	$[\bar{1}10]$	19·5	0·41	47·5	$2/(1-\chi_{12})$
	$[\bar{1}11]$	49*	0·83	59	$3/(1-\chi_{12}+\chi_{44})$

* Uncertain—near to centre of spot.

and the observed intensity, expressed in divisions of the chart, are given in Table 1.

Except for divergence and second-order thermal scattering corrections the value of $I(R/R_0)^2$ may be taken proportional to the K value. The divergence correction is fairly large for reflexions near the central spot and is taken into account finally. For the moment this is neglected. The second-order thermal scattering is quite certainly negligible because of the high values of the elastic constants. The following K ratio was found from the 'symmetrical' as well as the 'inclined' photograph:

$$K[010]_{440}/K[\bar{1}10]_{440} = \tfrac{1}{4}(1+1/\chi_{44})(1-\chi_{12})\,.$$

From the 'inclined' photograph only, the following K-ratio was found:

$$K[010]_{440}/K[001]_{440} = \tfrac{1}{2}(1+\chi_{44})\,.$$

These equations give $\chi_{12} = 0{\cdot}13$, $\chi_{44} = 0{\cdot}29$. This value of χ_{44} is the same as that of Voigt (1910) and of Doraiswami (1947). If we take $\chi_{44} = 0{\cdot}29$, and use the K ratio

$$K[010]_{440}/K[\bar{1}11]_{440} \text{ (symmetrical photo)}\,,$$

we obtain $\chi_{12} = 0{\cdot}07$.

If, however, we use the K ratio

$$K[001]_{440}/K[\bar{1}11]_{440} \text{ (inclined photo)}$$

we obtain $\chi_{12} = 0{\cdot}23$.

This last value is known to be uncertain because of the large divergence correction affecting the rekha $[\bar{1}11]$ near the centre. All the values of χ_{12} so obtained are positive and in the subsequent work a value of $\chi_{12} = 0{\cdot}085$ has been assumed.

Use of *K* surfaces

The information contained in the whole diffuse spot was utilized in the following manner. Assuming a set of c_{ik}'s consistent with the above analysis, namely $c_{11} = 37{\cdot}7$, $c_{12} = 3{\cdot}2$, $c_{44} = 10{\cdot}9$, a complete K surface was calculated, using the formulae given by Ramachandran & Wooster (1951). This is shown in Fig. 2, where the contours give the values of $K[ABC]_{440}$, in units of 10^{-13} cm.^{2} dyne^{-1}, since the K value has the dimensions of an elastic modulus. The surface was rotated through 66·7° about the [001] axis, so that the centre of the stereogram should correspond to the centre of the diffuse spot. The contours were then plotted on the same scale as the microdensitometer contours of Fig. 1(*a*). This is shown in Fig. 3(*a*). On top of this K-surface the circles corresponding to $(R_0/R)^2$ were drawn, as shown in Fig. 3(*a*). From this reorientated K surface the contours of the diffuse spot were worked out from the product of the K value and the value of $(R_0/R)^2$ at the same point. On the final diagram the value of $K[ABC]_{440}\times(R_0/R)^2$ is taken to be unity at the centre of the circles, and points are found for which the product is 0·7, 0·5, 0·3 respectively. Such a set of contours corresponds to what would be observed with an infinitely narrow parallel beam of X-rays. In fact, the Bragg spot when produced with about the same density as the diffuse spot had a vertical height of 1 mm. and a horizontal breadth of $\frac{1}{3}$ mm. approximately. A divergence correction to allow for this departure from an infinitely narrow and parallel beam was made as follows. A rectangle

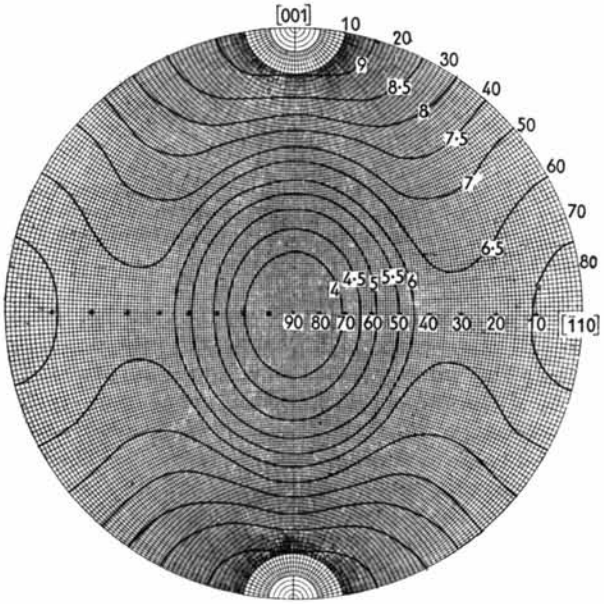

Fig. 2. Calculated K surface for 440, using the present values of the elastic constants.

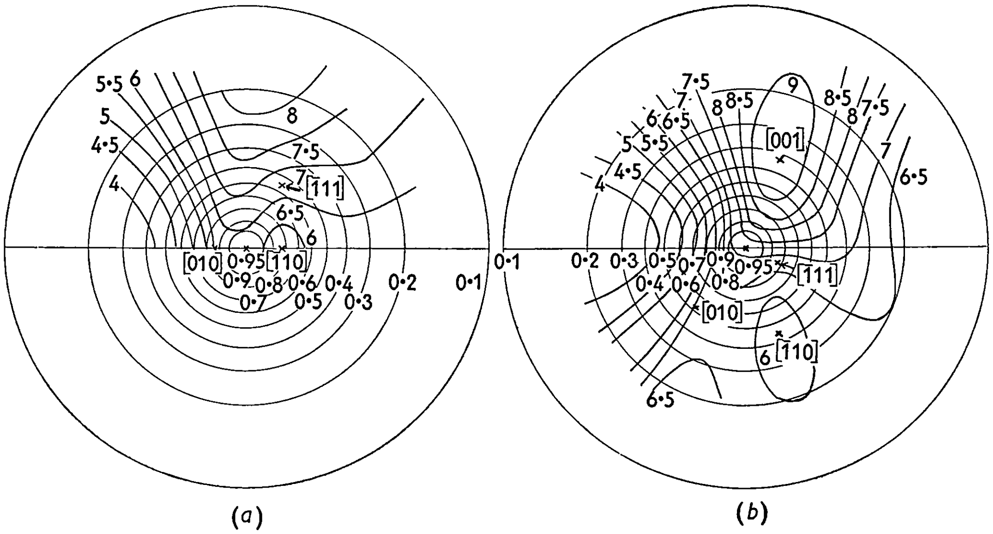

Fig. 3. (*a*) *K* surface rotated about [001] from right to left through 66·3° so that the centre of the *K* surface corresponds to the centre of the diffuse spot. The stereogram is plotted using the $\bar{\varrho}, \bar{\varphi}$ chart for $s = 0{\cdot}02$. The circles represent values of $(R_0/R)^2$. (*b*) *K* surface rotated clockwise through 45° and then from right to left about the vertical axis through 66·3° and plotted on the $\bar{\varrho}, \bar{\varphi}$ chart.

24×8 mm., corresponding to $1\times\frac{1}{3}$ mm. on the actual film, was superposed on Fig. 3(*a*) with the long edge vertical. The values of the calculated intensity at the centres of the three squares 8×8 mm. making up the whole rectangle were read, and the mean taken as the corrected value at the centre of the rectangle. This correction usually moves the 0·7, 0·5, 0·3 contours further from the centre but by less than a quarter of the distance between these consecutive contours. The calculated contours, corrected for divergence, are shown as broken lines in Fig. 1(*a*). The corresponding curves were calculated for the inclined photograph. The *K* surface shown in Fig. 2 was first rotated clockwise through 45° about the rel-vector [110], normal to the diagram, and then through 66·7° about the vertical axis so as to bring the *K* surface into the orientation corresponding to the photograph. This *K* surface was then transferred to the scale of the microdensitometer record by the method already described, and the result is shown in Fig. 3(*b*). The calculated contours, obtained as described above, are plotted as broken lines in Fig. 1(*b*).

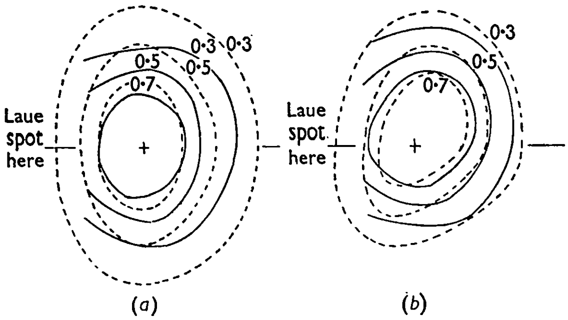

Fig. 4. (*a*) The observed density contours for the 'symmetrical' photograph are represented by the full lines, as in Fig. 1(*a*) The broken lines are the calculated contours using the former values of the elastic constants.
(*b*) The same applied to the 'inclined' photograph.

In order to make a comparison with the previous values of the elastic constants the calculations were repeated with $c_{11} = 36{\cdot}3$, $c_{12} = -4{\cdot}7$ and $c_{44} = 10{\cdot}5$ ($\chi_{12} = -0{\cdot}13$, $\chi_{44} = 0{\cdot}29$). The resulting contours are compared with the present observed intensity contours in Fig. 4. Figs. 1(*a*) and 4(*a*) give the comparison for the symmetrical photograph. The agreement is better in Fig. 1(*a*) than in Fig. 4(*a*) though the observed curves for 0·5 and 0·3 are smaller than the corresponding calculated curves. In Figs. 1(*b*) and 4(*b*) the comparison can be made for the inclined photograph. The calculated contours for the Doraiswami elastic constants are more elongated in a nearly vertical direction and the major axis of the figure is more inclined to the vertical in Fig. 4(*b*) than in Fig. 1(*b*). In both of these respects the new constants give better agreement than the previous values.

Conclusion

The cubic compressibility, β, (extrapolated to zero pressure), is given as $6{\cdot}80\times 10^{-13}$ cm.^{2} dyne^{-1} (Bridgman, 1949). Using the relation,

$$1/\beta = \tfrac{1}{3}(c_{11}+2c_{12})$$

and the elastic ratios $c_{12}/c_{11} = 0{\cdot}085$, $c_{44}/c_{11} = 0{\cdot}29$, we obtain the values already quoted, namely,

$$c_{11} = 37{\cdot}7,\ c_{12} = 3{\cdot}2,\ c_{44} = 10{\cdot}9\times 10^{11}\ \text{dyne cm.}^{-2}.$$

From these values of c_{ik}'s we obtain the following s_{ik}'s:

$$s_{11} = 2{\cdot}69,\ s_{12} = -0{\cdot}002,\ s_{44} = 9{\cdot}2\times 10^{-13}\ \text{cm.}^2\ \text{dyne}^{-1}.$$

Apart from the value 2·88 for s_{11} obtained by Voigt (1910), and the value 2·69 obtained by Doraiswami (1947), values have been given by Tutton (1922) (3·47) and by Birch (1950) (2·64). The present value of s_{11} therefore falls within the range observed by others.

The accuracy of the determination of χ_{44} is about ±0·04 if reasonable variations are allowed for possible error in determination of the density distribution on the photograph and in the determination of the position on the photograph corresponding to particular rekhas. The accuracy of the determination of χ_{12} is lower than that of χ_{44}. We may obtain an indication of the range of values of c_{12} consistent with the present observations from the different values of χ_{12} obtained from the photographs. The form of the contours in Fig. 1(*b*) is affected by the value of χ_{12} but not so markedly as to permit a precise determination of c_{12}. The roughly estimated range of possible values of c_{12} is $\pm 2 \times 10^{11}$, the mean value being 3×10^{11} dyne cm.$^{-2}$.

One of the authors (S. C. P.) feels a great pleasure in recording his gratitude to the Government of Bihar, India, for the grant of a research scholarship and the leave for the period in which this work has been carried out.

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Acta Cryst. (1956). **9**, 173

A Re-determination of the Structure of Triphenylene

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(*Received* 25 *July* 1955)

The structure of triphenylene derived by Klug is unconvincing because there are some large discrepancies between calculated and observed structure amplitudes, although the agreement residuals (0·20 for *hk*0 and 0·32 for 0*kl* reflexions) appear to be satisfactory. The present paper describes an independent attempt to derive the structure from Klug's data: the molecular orientation is found by means of optical-transform principles (and turns out to be the same as that found by Klug); the molecular position is found by means of Taylor's method, which is based upon selected zero or weak reflexions. A result different from that of Klug is obtained; it gives better agreement with the observed data and gives no anomalous intermolecular distances.

1. Reasons for re-determining the structure

The crystal structure of triphenylene described by Klug (1950) has some properties that cast doubt upon its validity. First, although reasonably low agreement residuals are reported (0·20 for *hk*0 and 0·32 for 0*kl* reflexions), there are some individual discrepancies that are too large to be accepted. The most prominent of these are shown in Table 1.

Secondly, some of the distances (e.g. 2·58 Å) between atoms in neighbouring molecules are too small to correspond to ordinary van der Waals forces (Robertson, 1953; Jdanov & Zvonkova, 1954; Vand & Pepinsky, 1954).

Table 1. *Some discrepancies in Klug's results*

hkl	310	330	350	430	440	021	031	074
$\|F_o\|$	61	54	19	< 5	38	22	< 4	10
F_c	20	−28	−10	−14	15	−6	20	26

It was therefore decided to see whether Klug's data could be satisfied by another structure, which would give at least as good general agreement as Klug's structure and would give no discrepancies comparable with those listed in Table 1. It was hoped that, if such a structure could be found, it would settle the problem of the anomalous distances.