A DETERMINATION OF THE PARAMETER
FOR HAUERITE

Thesis presented by
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In partial fulfillment of the requirements
for the degree of Master of Science

California Institute of Technology
Pasadena, California
1934

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Part I - Introduction

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Ia. Covalent Bonds, and Covalent Radii

The electron-pair bond was originally postulated by G. N. Lewis in 1916 as an explanation of covalency. Since the advent of the quantum mechanics, a much better understanding of the nature of the bond has been obtained. Heitler and London[1] and others have treated the hydrogen molecule by quantum mechanics. In the original treatment of Heitler and London, they considered simple resonance of the electrons between the two nuclei, with one electron always on each nucleus. This gives rise to what might be termed a pure covalent bond, It has been shown by Pauling[2,3] and others how this treatment may be extended to more complicated molecules. In general, we have bond formation whenever we have equivalence degeneracy; this is the justification of the electron-pair bond, for indistinguishable states are had if we consider the first electron of the pair on the first nucleus, and the second electron on the second, or vice versa.

In this simple treatment, however, the possibility is neglected of both electrons being on one nucleus at the same time; that is, the possibility of ions existing is ignored. To determine the approximate contribution of the ionic character to the total state of the molecule, we can set up the wave function having the correct symmetry properties, as was done by Weinbaum[4] for the hydrogen molecule:

$$\alpha\left[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)\right] + \beta\left[\psi_a(1)\psi_a(2) + \psi_b(1)\psi_b(2)\right]$$

(covalent term) (ionic term)

Here, ψ_a, ψ_b are wave functions about nuclei a and b, respectively, and (1) (2), indicate the electron considered. The parameters, α, β are varied so that the resultant energy is a minimum; this has been shown[5] to give the best wave function of the type. Then, presumably, the ratio $\frac{\beta^2}{\alpha^2}$ gives, at least approximately, the relative contributions of ionic and covalent character to the state of the molecule.

The exact distinction between ionic and covalent bonds is necessarily somewhat arbitrary, in as much as the wave functions corresponding to the normal and all excited states of an ion form a complete orthogonal set, so that any wave function, even one that is purely covalent in the sense used above, can be accurately represented as a series expansion of the ionic functions. Pauling[6] therefore prefers to consider in an approximate treatment only the wave functions corresponding to ions or atoms in their lowest states. He then defines a normal covalent bond as one in which ionic terms of the wave functions for each atom occur with the same coefficient. Bonds in molecules of the type H:H, discussed above, are necessarily normal covalent, from considerations of symmetry. In addition, we may have bonds in molecules of the type A:B which are of this type, if A and B are of the same degree of electronegativity. Then terms corresponding to the states A^+B^-, and A^-B^+ will occur with the same coefficient. The bond in HI is very nearly purely normal covalent. That in NaCl, on the other hand, is largely ionic.

There are several considerations which enable one to distinguish between covalent and ionic bonds in many substances. For example, certain spatial arrangements of covalent bonds are to be expected[3], and we might expect molecules having these configurations, as determined by crystal structure investigations, to be largely covalent.

Pauling and Huggins[7] have prepared a table of covalent radii of atoms. They base their radii on observed values from crystal structure and band spectral data, with wave mechanical foundations To obtain the radii of tetrahedral atoms, theyfirst took (C)*, (Si), (Ge), and (Sn) as one half the observed interatomic distances in the diamond type crystals of those elements. They next took (S) as one half S-S* as determined from pyrite, FeS_2, and hauerite, MnS_2. From the values reported for S-S in these substances, (see next section), the value of (S) was taken as 1.06 Å. Having this value, the radii of a number of other atoms could be determined from their respective sulfides, by subtracting this value of (S) from theiobserved interatomic distances. The best smaooth curves were then drawn for each row of the periodic table, tetrahedral radius versus atomic number. It was then noticed that the atomic radius as read from these curves for the halogens differed considerably from the values given by band spectral data. The values read from the curves were about

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* The symbol (C) means the covalent C radius; and S-S means sulfur - sulfur distance, etc.

0.02 Å too small for (I), while (Cl) and (F) were each about 0.01 Å too large. As it seemed doubtful that the directions of the discrepancies should be different in Cl and I, the value of (S) was assumed to be 1.04 Å, and all the calculations repeated. This gave perfect agreement for (Cl) and (F), while some discrepancy in (I) and (Br) was attributed to the difference in the orbitals involved in the bonds. Pauling and Huggins considered the difference between the observed value for (S) and that required by their table to indicate that the sulfur radius might be dependand on the nature of the crystal.

The divalent manganese radius was estimated by the extrapolation: Ni^{II}(1.39 Å); Co^{II}(1.32Å); Fe^{II}(1.23 Å), to be 1.15 Å. Also, by extrapolation of the isoelectronic sequence,

Ni^{IV}(1.21 Å); Co^{III}(1.22 Å); Fe^{II}(1.23 Å)

an upper limit of 1.24 Å is placed on (Mn^{II}). However. the obseved value of MnS in hauerite, as calculated from Ewald and Friedrich's value of the parameter (which is discussed later) is 2.58 Å, giving (Mn^{II}) as 1.55 Å, and from $MnTe_2$, it is found to be 1.59 Å. Paulin and Huggins could offer no explanation of this anomalously large radius.

It seems worth while to investigate whether the discrepancy, 1.06 vs. 1.04 Å for (S) is real, as suggested by Pauling and Huggins, who made the suggestion that it results from a change in the orbitals), or is due to error in the reported value of the parameter. In view of this, and of the anomolously manganese radius, I have reinvestigated crystal hauerite. In the following sections there is given a discussion of previos work, with an estimation of errors, and a description of the method used in my work, and in Part II, an account of my parameter determination. The result odtained is that I find for hauerite the parameter value $u = 0.4012 \pm 0.0004$, the S-S distance, 2.086 ± 0.01 Å, and the S radius, 1.043 ± 0.005 Å. The manganese radius is unchanged.

Ib. Early Work

The crystal structure of pyrite was first worked out by W. L. Bragg[8], by the use of his spectrometer, as one of his early structure determinations, and the first involving a parameter. He attributed to the crystal a symmetry which would place it in the space group T_h^6. The Fe atoms lie on a face-centered cubic lattice. If we pass planes, parallel to the cube faces, thru each Fe atom, we obtain eight small cubes from the unit cube. We now draw diagonals of these eight cubes in such a way that none intersect. Each diagonal will have an Fe atom at one end, and an empty corner at the other, A S atom is placed on each diagonal at a distance $ua_0\sqrt{3}$ from the Fe atom at the end of the diagonal. a_0 is the length of the edge of the unit cube; $a_0\sqrt{3}$ is thus the length of the diagonal of the unit cube, and u is a parameter to be determined experimentally. The structure is illustrated in Fig. 1. For clearness, the cube has been represented as divided into halves. The lettering indicates how the

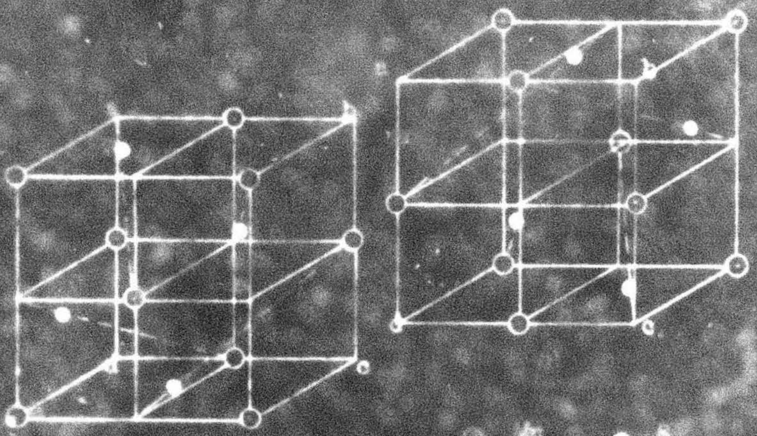

Figure 1

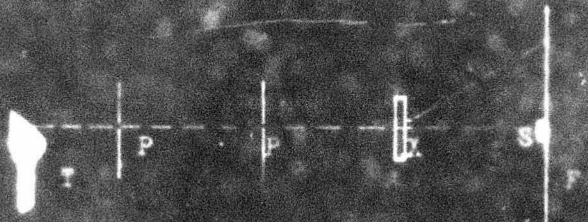

Figure 2

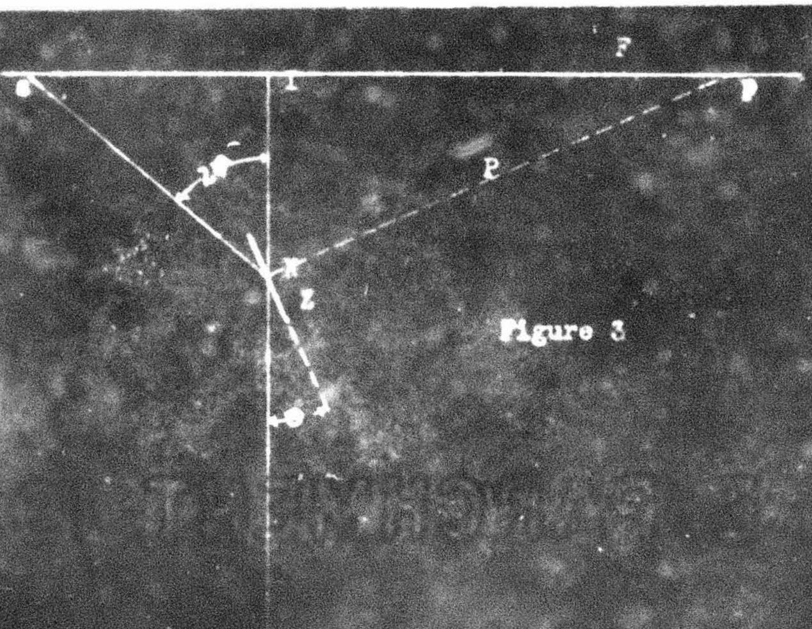

Figure 3

halves are to be joined. Bragg believed from his spectral intensity intensity measurments that u was between 0.395 and 0.405.

Shortly after the work of Bragg, Ewald and Friedrich[9] reëxamined pyrite by means of Laue photographs, which had been first taken about a year previously by Friedrich and Knipping, at the suggestion of Laue. In this method, continuous, or "white" X radiation is sent thru the crystal, in contrast to the method of Bragg, in which monochromatic radiation is reflected from a crystal face.

As a result of their work, which I shall discuss more fully in the next section, Ewald and Friedrich came to the conclusion that Bragg's value for the parameter in pyrite is slightly too high. They assigned to u a value between 0.3875 and 0.3885. In addition, they examined hauerite, which is isomorphous with pyrite, and assigned to it a parameter value of 0.4000 ± 0.0005. As mentioned before, my investigation indicates this to be in slight error.

Parker and Whitehouse[10] redetermined the parameter for pyrite, obtaining a value of 0.386, but their value is probably not as accurate as that of Ewald and Friedrich, for it was obtained by Fourier analysis of the crystal.

Ic The Laue Method

The set up used in preparing Laue photographs is shown diagramatically in Fig. 2. Radiation from the target T of the X-ray tube is collimated by two pin holes, P,P. It is then passes thru a thin section of the crystal, X, and the scattered and undeflected rays strike the photographic plate, F. A small shield, S, is usually placed before the plate to intercept the undeflected ray, to prevent the formation of an overly intense central image.

It is easily shown that if we have a series of identical parallel planes thru points of the crystal lattice, separated by a distance d from one another, then a ray incident to the planes at an angle θ will be reflected by the series of planes if the wave length of the ray and the angle of incidence satisfy the relation

$$n\lambda = 2d \sin\theta \qquad (1)$$

where n is any integer. The angle of reflection is, as usual, equal to the angle of incidence. In a cubic crystal, the distance between such reflecting planes of indices (hkl); that is, intersecting the crystallographic axes at distances proportional to 1/h, 1/k, 1/l, is easily shown to be

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \qquad (2)$$

The condition for reflection from such a plane is thus that

$$n\lambda = \frac{2\, a_0 \sin\theta}{\sqrt{h^2 + k^2 + l^2}} \qquad (3)$$

But the radiation used in preparing Laue photographs is "white", and contains radiation of all wave lengths greater than the cut-off provided by the quantum condition,

$$eV \geqq h\nu$$

or

$$eV \geqq \frac{hc}{\lambda}$$

where e is the charge on the electron, and V the potential applied to the X-ray tube. Thus, provided

$$\frac{2\,a_0 \sin\theta}{\sqrt{h^2 + k^2 + l^2}} \geqq \frac{hc}{eV} \qquad (4)$$

the set of planes (hkl) will always give a reflection.

If we take some point of the space lattice as origin, then the direction in space of a line passing thru the origin may be represented by the coordinates x,y,z, of some other point thru which the line passes. If x,y,z, bear a rational relationship to one another, the line passes thru a point u,v,w, where u,v,w, are all integers. Then, in general, there are a large number of planes passing thru this line and intercepting other lattice points. All these planes form a <u>zone</u>, and the line is termed a <u>zone axis</u>, and designated by the indices [uvw].

If (hkl) and (h'k'l') are two of the planes in the zone, the indices of the zone axis may be shown to be given by

$$u = kl' - lk'$$

$$v = lh' - hl'$$

$$w = hk' - kh'.$$

In a similar manner, as two straight lines determine a plane, the indices of a plane passing thru the zone axes [uvw] and [u'v'w'] may be shown to be

$$h = vw' - wv'$$

$$k = wu' - uw'$$

$$l = uv' - vu'.$$

Now, for every plane in a zone, there is a large number (infinite, for an infinite lattice) of identical parallel planes at distances given by (2). Then, a ray passing into the lattice will be reflected by each of the planes of the zone, and this multiplicity of reflections will form a circular cone of rays, with the zone axis as the axis of the cone, and the undeflected ray will lie on the cone. Figure 3 represents such a zone axis, Z. The plate, P, will cut the generated cone, and as is well known, the intercept of the cone on the plates will be an ellipse; thus, all the reflections of a given zone lie on an ellipse passing thru the central image, I.

If we construct the perpendicular P to all the planes of the zone, they will evidently all lie in a plane, and this plane will, of course, intersect the plate in a straight line. Thus, if we make a plot from the Laue photograph to convert from the observed positions of reflections from a plane to that of the intercept with the perpendicular to a plane, the ellipses are converted to straight lines -- a great aid in assigning indices to the reflections, and interpreting the photograph. This is termed a "gnomonic projection". To make this plot we notice that, if IX is the crystal to plate distance, Is the distance from reflection to central image, and Ip the distance from the projection to central image, then

$$Is = IX \tan 2\theta$$

$$Ip = IX \cot\theta .$$

IX is usually fixed at 5 cm. In plotting the gnomonic projection, it is convenient to use a gnomonic ruler, which converts the distance Is directly to Ip, and gives the value of sin θ for the reflection.

When the indices and sin values are assigned to all the reflections, it is usually possible to get an approximate value for a_0; for we can take the smallest value of $\frac{\sin\theta}{\sqrt{h^2 + k^2 + l^2}}$ found, and substitute it in relation (4), and then the smallest value of a_0 for which the relation holds provides a lower limit for a_0. If a large number of reflections are present, it is often possible to obtain a fairly accurate value; at least accurate enough that the number of molecules in the unit cell can be given. Then, from a knowledge of the density, the chemical composition, the atomic weights of the constituents, and Avogadro's number, it is possible to assign a more accurate value to a_0. For greatest accuracy, however, the size of the unit is obtained from oscillation photographs or spectrometric measurments. When the size of the unit has been determined, it is possible to assign $n\lambda$ values to every reflection by substitution in (3). If the value of $n\lambda$ for a reflection lies between the short wave cut-off for the radiation, and twice this value, it is evident that n must be unity; that is, the reflection is first order. For reflections of greater $n\lambda$, it is impossible to assign the order of the reflection.

Altho some information concerning the structure of a crystal is to be had from the symmetry of Laue photographs, to get complete information, it is necessary to make intensity comparisons. The equation of a plane (hkl) thru the point x_j, y_j, z_j is

$$\left[hx + ky + lz - \frac{hx_j + ky_j + lz_j}{\sqrt{h^2 + k^2 + l^2}}\right]a_0 = 0$$

The distance of this plane from the origin is

$$\frac{hx_j + ky_j + lz_j}{\sqrt{h^2 + k^2 + l^2}} = op_j$$

For reflection, the phase difference for identical planes (hkl) must be 2wn. The distance between identical planes was given (eq. (2)) as

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

Then the phase difference ψ_j of a wave reflected from the planes (hkl) identical with that thru x_j, y_j, z_j, and a wave reflected by planes identical with that thru the origin is given by

$$\frac{\psi_j}{2wn} = \frac{op_j}{d_{hkl}} = \frac{\frac{hx_j + ky_j + lz_j}{\sqrt{h^2 + k^2 + l^2}}\,a_0}{\frac{a_0}{\sqrt{h^2 + k^2 + l^2}}} = hx_j + ky_j + lz_j$$

and

$$\psi_j = 2wn(hx_j + ky_j + lz_j)$$

It is shown in the theory of wave motion that the amplitude F of the resultant of a number of waves of the same frequency, and of amplitudes $f_p, f_q, \ldots\ldots$, and phases $\psi_p, \psi_q, \ldots$, is given by

$$F = f_p \exp i\psi_p + f_q \exp i\psi_q + \cdots$$

Thus, putting in the expression for the phase found above, the amplitude of the resultant wave reflected by all planes parallel to (hkl) is found to be proportional to

$$F = \sum_j f_{o_j} \exp i2\pi n(hx_j + ky_j + lz_j)$$

Here, x_j, y_j, z_j, are the coordinates of the j^{th} atom in the unit cell, and f_{o_j} the scattering power of the j^{th} atom, called the "atomic scattering factor" of the atom. Assuming the atoms to be spherically symmetrical, the atomic scattering factors are functions of the nature of the atom, and of $\sin\theta/\lambda$. They have been tabulated for all atoms for various values of $\sin\theta/\lambda$. F is termed the "structure factor". The intensity of the reflection is proportional to FF^*. In calculating intensities, it is usually more convenient to convert the exponential to the triginometric form:

$$\exp i2\pi n(hx_j + ky_j + lz_j) = \cos 2\pi n(hx_j + ky_j + lz_j) + i \sin 2\pi n(hx_j + ky_j + lz_j)$$

The actual amplitude of the reflected beam depends in a complicated way on a number of other factors, such as θ and λ, but if comparisons are only made between reflections for which all these other factors are constant, it is sufficient to use only the F values in comparison.

IId A Discussion of the Parameter Determination of Ewald and Friedrich

Ewald and Friedrich in their work on hauerite referred to above, carried thru the method essentially as described above, tho they didn't attempt to fix the size of the unit cell. In their determination, they found that the reflection $(52\bar{1})$ does not appear. As the structure factor for this reflection disappears for u = 0.4, they took this as the value of u. They considered their results to be accurate within 0.0005. However , as the structure factor for $(52\bar{1})$ increases but slowly on either side of its point of disappearance, and especially as the intensity of reflection is proportional to the square of the structure factor, this is not a very sensitive method for determining the value of u. The reflection probably would not be observed even if u differed as much as 0.0015 from the value 0.4000, for the intensity of $(52\bar{1})$ would still be only between one two-hundredth and one three-hundredth that of $(25\bar{1})$, a reflection of medium intensity.

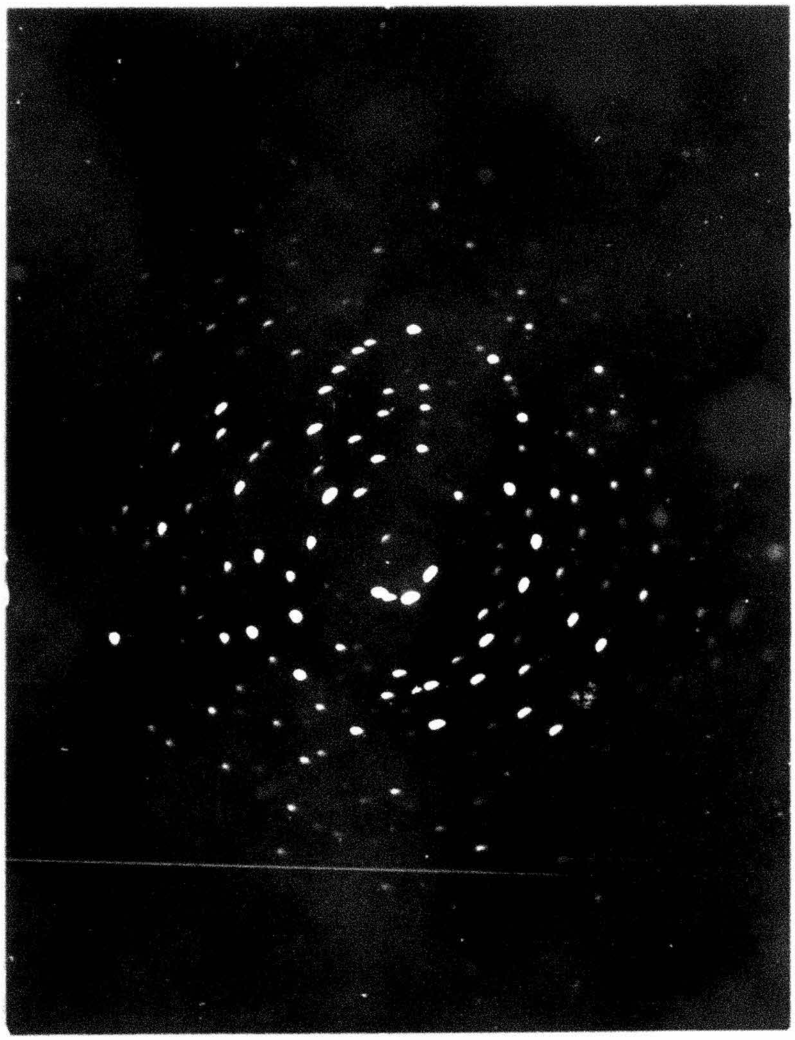

Figure 4

Part II A New Parameter Determination for Hauerite

In this part is described a new determination of the parameter for hauerite which I have carried out by the use of the Laue method.

The size of the unit of structure of hauerite has been measured a number of times. Pauling and Huggins[7] give $a_0 = 6.097 \pm 0.005$ Å, as determined from oscillation photographs. I have used this value of a_0 in the present determination.

A Laue photograph was prepared with the incident beam nearly normal to (111). The photograph so obtained gave a large number of well shaped spots. Figure 4 is a print made from the photograph. Upon making a gnomonic projection, assigning indices, and calculating n for the reflections, no spots with $n\lambda$ less than 0.24 Å, the short wave cut-off of the radiation used, were found. There is, therefore, no indication that the unit is larger than previously reported.

If hauerite has the pyrite structure, its space group is T_h^6. This requires first order reflections with indices (0kl), with k odd, to be absent*. Several such reflections were found, but all but one of these were very faint, and all were shaped differently from the other spots on the photograph. The one fairly strong spot was $(0\bar{3}4)$, which was at $n\lambda = 0.38$ Å. $(40\bar{3})$, which is of the same form as $(0\bar{3}4)$, and would fall at $n\lambda = 0.39$ Å, was absent. Therefore, if the reflection $(0\bar{3}4)$ is real, the crystal could not be cubic. This is highly improbable.

In general, only intensities of reflections of nearly the same nλ, and the same interplanar distance were compared. In this way, the calculations were much simplified, for the ratio of the intensities of two such reflections is just the square of the ratio of their structure factors.

The atomic positions in MnS_2, assuming the space group T_h^6, are:

Mn: 0,0,0; 1/2,1/2,0; 1/2,0,1/2; 0,1/2,1/2.

S: u,u,u; $1/2+u, 1/2-u, \bar{u}$; $\bar{u}, 1/2+u, 1/2-u$; $1/2-u, \bar{u}, 1/2+u$.

$\bar{u},\bar{u},\bar{u}$; $1/2-u, 1/2+u, u$; $u, 1/2-u, 1/2+u$; $1/2+u, u, 1/2-u$.

The structure factor for the reflection (hkl)*, with h,k, andll all odd is then, for first order reflections,

$$F = 4\,f_{Mn} + 8\,f_S \cos 2\pi hu \cos 2\pi ku \cos 2\pi lu,$$

and for h,k even, l odd; or h,k odd, l even,

$$F = 8\,f_S \cos 2\pi hu \sin 2\pi ku \sin 2\pi lu.$$

The f_o values used are those given by Pauling and Sherman[11]. It is to be noticed that in comparing the intensities of two reflections of the same interplanar distance, and where F for both reflections is given by the second equation above, the scattering factors do not enter into the expression for the relative intensities of the two reflections. The use of such comparisons makes possible a more accurate parameter determination, for uncertainties in f_o values will then not effect the results.

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* Because of the symmetry of the group, planes involving cyclic interchange of the same indices are of the same form.

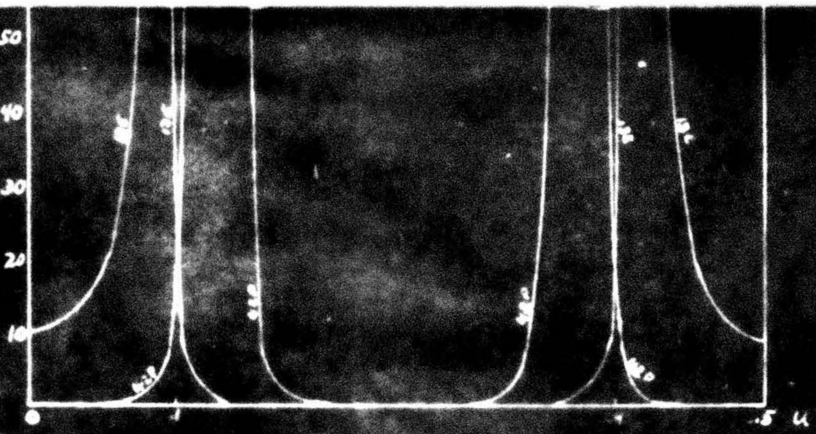


Figure 5

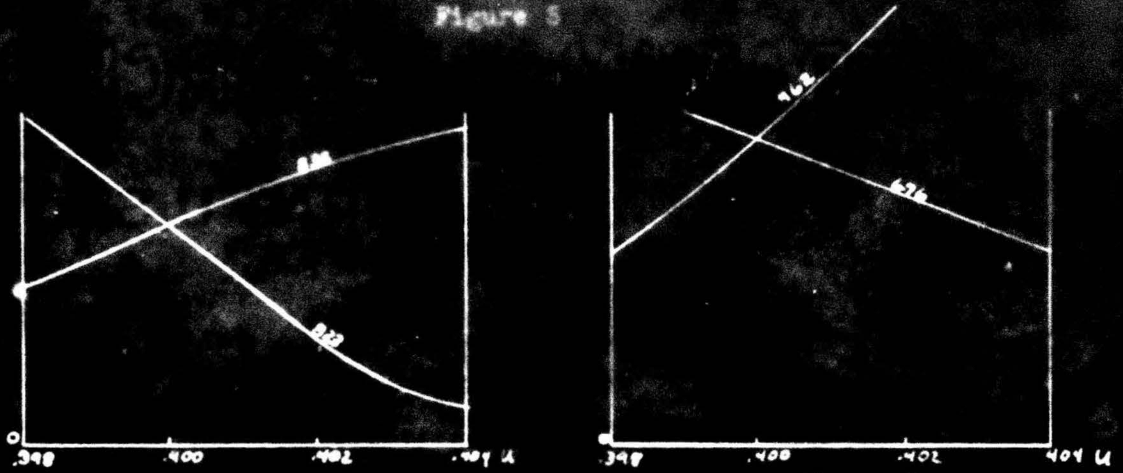
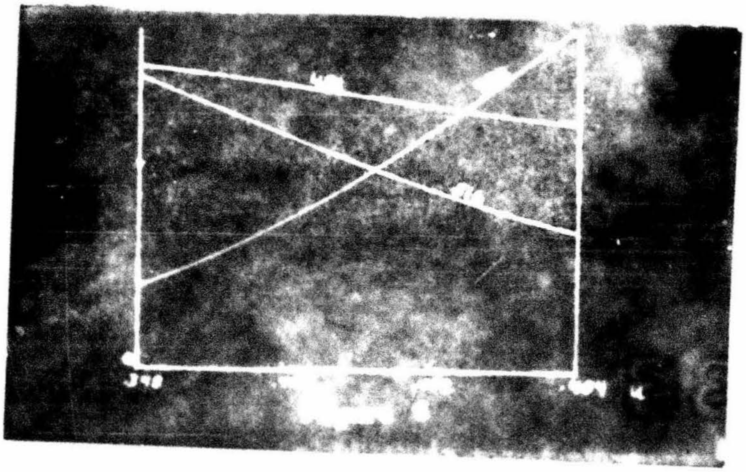


Figure 6

Figure 7



The parameter was quickly narrowed down to the region near 0.4 by the comparisons (42P) - (24P), where P is any odd integer, and (13E)-- (31E), where E is any even integer. The ratios $F^2(42P)/F^2(24P)$, and $F^2(13E)/F^2(31E)$ are plotted in Figure 5 against the parameter, u. All intensities are symmetrical about u = 0.5, so the curves have only been plotted from 0.to 0.5. The approximate observed values were,

I(421)/I(241) = 12 I(427)/I(247) = 8
I(423)/I(243) = 15
I(134)/I(314) = 18 I(136)/I(316) = 9

It will be observed that the only places where both curves agree with the observed values are in the regions u = 0.095 to 0.105, and u = 0.395 to 0.405. The ratio of I(535) to I(614), which is observed to be about 10, definitely shows that u must lie in the neighborhood of 0.4, for the calculated ratio, $F^2(535)/F^2(614)$ is 1.45 for u = 0.1, and 11.6 for u = 0.4.

A fairly large number of comparisons were used in determining u more closely. Those used in the final determination are listed below:

Index	nλ	$I_{obs.}$	R*
832	0.372	0.30	1.6
823	0.362	0.18	
962	0.376	0.15	1.4
676	0.365	0.10	
481	0.308	0.35	1.3
732	0.341	0.40	1.0
651	0.354	0.48	

*Ratios corrected for difference in nλ

The approximate correction for difference in nλ was made by plotting a curve of $I_{obs.}$ vs. nλ for the various reflections of the same form falling at different values of $n\lambda$. The squares of the structure factors are plotted from u = 0.398 to u = 0.404 in Figures 6, 7, and 8. Each of the comparisons (832) - (823) and (962) - (676) rigorously limits u to values above 0.4000. Also, altho (481) is at greater interplanar distance than (732), it is of greater intensity (when corrected for difference in $n\lambda$), and therefore its F^2 value must be greater than that of (732). As seen from Fig. 8, this establishes a definite upper limit for u at 0.4026. From the comparisons (832) - (823), it is seen that u probably lies between 0.4008 and 0.4016. The comparison (962) - (676) indicates a value of u between 0.4008 and 0.4020. The last comparison, (651) - (732) gives a value of u from 0.4006 to 0.4016. This is probably the most useful comparison for the exact determination of the parameter. From a consideration of all these comparisons, the value of the parameter has been taken as

$$u = 0.4012 \pm 0.0004$$

The limits given are the probable error. Using this value for u, and the value for a_0 given before, the S - S distance is found to be 2.086 ± 0.01 Å, giving a bond radius for S of 1.043 ± 0.005 Å, in good agreement with the value taken by Pauling and Huggins. This small change in the parameter, however, leaves the Mn - S distance practically unchanged at about 2.59 Å, thus leaving Mn with the anomalous radius of about 1.55 Å.

This problem was suggested by, and carried out under the direction of, Prof. Linus Pauling, to whom I am indebted for much invaluable aid.

Summary

In Part I, after a discussion of covalency and covalent radii, a brief review of the work of Bragg on pyrite, and Ewald and Friedrich on pyrite and hauerite, with an evaluation of accuracy, is given. The Laue method for crystal analysis is described, and the theory outlined.

Part II is devoted to the description of a new parameter determination for hauerite carried out by the writer. As a result of this determination, the parameter has been fixed at

$$u = 0.4012 \pm 0.0004,$$

giving a covalent sulfur radius of 1.043 Å.

Addenda

Since the previous was written, another Laue photograph has been prepared from a new crystal of hauerite. On this photograph, no reflections of the type (0kl), with k odd, were present. It is thus quite certain that the presence of such reflections on the previous photograph was due either to imperfections in the crystal, or to twinning.

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