ter (50:30:14:6). In both cases the devel-
opment was started immediately after the
addition of solvent, and without tank
saturation.

For the detection of the amino acids on
the chromatogram a ninhydrin-collidine
reagent was used. The reagent consisted of
ninhydrin (0.15 g), acetic acid (10 ml) and
2,4,6-trimethyl-pyridine (1.25 ml), made
up to a final volume of 50 ml with ethanol.[2]
After spraying, the plates were placed on
a hot plate (125°C) and the shape and
colour of the spots marked with a pencil
as they appeared. Not only was identifica-
tion possible from the positions of the
spots, but the process was also made easier
by noting the speed of development, inten-
sity and shade.

In addition to the 23 amino acids resolved
by Jones and Heathcote, the system also
provides a separation for norleucine, β-
alanine, 4-aminobutyric acid, and 2-ami-
noglucose, some of which are present in
complex humic hydrolysates. Norleucine
(9.3, 5.9) is positioned close to, but defi-
nitely separated from, leucine (9.2, 5.4) and
isoleucine (8.9, 4.8), where the parentheses
give the R_F values for the first and second
dimensions. β-Alanine (5.0, 1.1) and α-ala-
nine (6.1, 1.3) separate well, but the latter
may be partly overlapped by 4-aminobutyric
acid (5.8, 1.2) which is positioned between
them. Nevertheless all three can be recog-
nized when present together in about equal
amounts. 2-Aminoglucose (2.9, 3.3) is situ-
ated near serine (3.3, 1.8), but well sepa-
rated from it.

According to the technique outlined
above, we have analysed samples arising
from different treatments of raw humus.
The system works satisfactorily and also
resolves several ninhydrin-positive spots
which could not be assigned to any of the
compounds mentioned above.

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Redetermined Crystal Structure of FeS₂ (Pyrite)

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The crystal structure of pyrite (FeS_2) was
one of the very first to be determined by
the method of X-ray diffraction. This early
(1914) work by Bragg[1] and Ewald and
Friedrich[2] depended on the use of single
crystals, as are required by the Laue
method. Suitable crystals were available in
the form of the mineral pyrite. The only
redetermination of this structure on the
basis of an improved single crystal tech-
nique was reported in 1932 by Parker and
Whitehouse,[3] whereas other investigators
have employed various powder techniques
on natural as well as synthetic samples.

Chemical intuition and elementary semi-
theoretical considerations led Pauling and
Huggins[4] (see also Pauling[5]) to suggest
that the shortest (*i.e.* bonding) interatomic
Fe−S and S−S distances in the pyrite and
marcasite modifications of FeS_2, respec-
tively, should be virtually equal. These
expectations were found[4] to be confirmed
with respect to the bonding Fe−S dis-
tances (which at that time were reported
to be identical), whereas the short S−S
pair distance appeared to differ consider-
ably (2.09−2.14 Å *versus* 2.25 Å, respec-
tively) between the two modifications.
According to their empirical scheme of
tetrahedral radii, Pauling and Huggins[4]
furthermore deduced a predicted S−S
distance of 2.08 Å, which together with the
above evidence led them to propose that
the parameter values for marcasite re-
ported by Buerger[6] were probably inaccu-
rate. Provoked by this criticism,[4,7] Buer-
ger[8] repeated the determination of the
marcasite structure and confirmed his
original[6] parameter values with improved
accuracy. However, the question concerning
the distinction between the S−S pair
distance in pyrite and marcasite remained
unresolved, since the positional parameter
of the pyrite structure might equally well
be inaccurate. This view is in fact sup-
ported by the scattered values reported
over the years for the S−S pair distance in
pyrite (ranging from 2.09 to 2.17 Å, the
latter value by Elliott[9] being the most

recent), thus leaving the value uncertain, even up to the present. It therefore appeared to be of considerable interest to attempt a definitive redetermination of the structure by a single crystal technique and the use of modern computing and correction methods.

Single crystals of FeS_2-p were prepared by chemical transport reactions, using iodine ($\sim$1 mg/ml capsule volume) as the transport agent. A good yield of suitable crystals was obtained by applying a temperature gradient of $\sim$1°C/mm along a $\sim$200 mm long (evacuated and sealed) silica capsule, with the hot end containing a stoichiometric mixture of the elements (99.99+ % Fe from Johnson, Matthey & Co., Ltd. and 99.9999 % S from Koch-Light Laboratories, Ltd.), at 620°C. These conditions produced a considerable number of crystals at the cold end of the capsule after 5 days.

The majority of the crystals were shaped as rectangular prisms, which showed a large variation in proportions. The crystal selected for the present study had the dimensions $0.07 \times 0.04 \times 0.03$ mm, the crystallographic axes being parallel to the edges of the crystal. X-Ray photographs were taken in an integrating Weissenberg camera of 57.3 mm diameter with Mo$K\alpha$-radiation using the multiple-film technique and the intensities were measured microphotometrically except for the weakest reflections which were estimated visually. The intensities were corrected for the combined Lorentz and polarization factors, and for absorption and secondary extinction according to the actual shape of the crystal. Atomic scattering factors were taken from Hanson et al.[10] and the corrections and refinements were carried out according to programmes by Dahl et al.[11]

The dimension $a = 5.4179 \pm 0.0011$ Å * of the cubic unit cell of FeS_2-p (deduced from Guinier photographic data of crushed crystals according to the method of least squares) is in perfect agreement with the value recently reported by Bither et al.[12] for a synthetic sample. FeS_2-p assumes the stoichiometric 1:2 composition without having any appreciable range of homogeneity and the unit cell contains four formula units. The systematic extinctions of reflections of the type $0kl$ for $k = 2n+1$ ($h0l$ for $l = 2n+1$ and $hk0$ for $h = 2n+1$)

* Throughout this paper the indicated error limits correspond to the standard deviations.

in the diffraction data, imply that the space group is $Pa3$.

The pyrite structure has been confirmed in several independent studies (cf. Refs. 1−3,9) and its essential features are clearly correct. Accepting that the space group is precisely established from the systematic extinctions, there are one positional parameter and two temperature factors to be determined for this structure.** The least squares refinements converged very rapidly to the following parameter values:
Fe in $4(a)$ with $B = 0.14 \pm 0.04$ Å²;
S in $8(c)$ with $x = 0.3840 \pm 0.0005$,
$B = 0.12 \pm 0.05$ Å², with $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0.075$. (The unobserved reflections are not included in the least squares refinements and the R-value.)

The present value for the positional parameter is identical with that derived by Elliott[9] from powder data. Despite the fact that Elliott was unable to use an objective criterion in assessing the probable error in the determination, it is worth noting that his error limits correspond to twice the standard deviation obtained in the present study.

The present values for a and x lead to the following bonding interatomic distances and relevant angles in pyrite:

Fe−S(6) 2.262 ± 0.003 Å
S−S(1) 2.177 ± 0.004 Å
S−Fe−S(6+6) $85.57 \pm 0.10°$
               $94.43 \pm 0.10°$
Fe−S−Fe(3) $115.71 \pm 0.12°$
S−S−Fe(3) $102.13 \pm 0.13°$

The length of these distances may be compared with the corresponding values obtained[14] for marcasite:

Fe−S (2+2+2) 2.230 ± 0.006,
               2.235 ± 0.002,
               2.275 ± 0.006 Å;
               average 2.247 Å
S−S(1) 2.223 ± 0.003 Å

It is seen that both the bonding Fe−S and S−S distances differ significantly between the two modifications, although the difference between the S−S distances in the two structures is rather less than was

** This neglects the possibility of infinitesimal deviations from the symmetry of space group $Pa3$. A reduction of the symmetry to that of space group $P2_13$ would, for example, provide virtually the same atomic arrangement, with a slight modification of the pyrite structure towards that of ullmanite (NiSbS).[13]

considered to be the case at the time of the controversy between Pauling and Huggins [4],[7] on the one hand and Buerger [6],[8] on the other (*vide supra*). These differences between the two modifications, which are related to the structural dissimilarities, will be subject to discussion in a forthcoming paper.

As a consequence of the cubic symmetry of the pyrite type structure and the fact that there is only one positional parameter, knowledge of the lattice constant a and estimates of the length of the bonding $X-X$ $(a\sqrt{3}(1-2x))$ or $T-X$ $(a(3x^2-2x+\frac{1}{2})^{\frac{1}{2}})$ distance enables prediction of the value of x (*cf.*, *e.g.*, Pauling and Huggins [4]). More conveniently, however, the value of x may be estimated from the ratio between these distances $(\sqrt{3}(1-2x)/(3x^2-2x+\frac{1}{2})^{\frac{1}{2}})$, since it may be easier to judge this quantity with reliability. (In the relevant range of x, *i.e.* $0.35<x<0.42$, the ratio can to a good approximation be simplified to the linear function $4.4454-9.0722x$.)

Substitution of the observed distance ratio for the marcasite modification of FeS_2 in the above expression, gives $x=0.381$ for pyrite, which accords reasonably well with the experimental value 0.3840. Similarly, the recent values for the distance ratios in the marcasite modifications of $FeTe_2$, [14]$CoTe_2$, [14] and β-$NiAs_2$ [15] may be utilized for the prediction of the x-values 0.364, 0.367, and 0.377, respectively, for the corresponding modifications with the pyrite type structure which have recently been prepared [12],[16] by high pressure syntheses. The hitherto unobserved pyrite variant of $NiSb_2$ may be predicted to have $a=6.204$ Å and $x=0.367$ on the basis of the structural data [15] for the marcasite modification. It must be emphasized, however, that these predictions are subject to some uncertainty (in particular in the latter case) since, *e.g.*, the size of transition metal atoms appears to correlate with their localized configurations of unpaired electrons (*cf.* Pearson [17]).

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New Metal-rich Arsenides of Niobium and Tantalum

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In several earlier investigations of the $Nb-As$ and $Ta-As$ systems,[1-7] the method of synthesis has been the direct reaction between the component elements at temperatures up to 1000°C. Under these conditions the only intermediate phases formed in each system are a monoarsenide and a diarsenide. Ganglberger,[8],[9] who employed higher temperatures for his syntheses, was able to prepare the metal-rich compounds Nb_3As and Ta_3As, both of which were reported to crystallize with the Ti_3P-type structure.

In the present paper, some results are reported from an examination of the

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