Table 1. *Crystal-structure data*

		Data for unit cell referred to rhombohedral symmetry		
Temp. (°K.)	Symmetry	a_R (A.)	α	Unit-cell volume (cm.^{3})
295	Cubic $a_0 = 8{\cdot}3940 \pm 0{\cdot}0005$ A.	$5{\cdot}9370 \pm 0{\cdot}0005$	60°	$24{\cdot}96 \times 10^{-24}$
165	Cubic $a_0 = 8{\cdot}3905 \pm 0{\cdot}0005$ A.	$5{\cdot}9345 \pm 0{\cdot}0005$	60°	$24{\cdot}89 \times 10^{-24}$
95	Rhombohedral	$5{\cdot}938 \pm 0{\cdot}001$	59° 50′	$24{\cdot}90 \times 10^{-24}$

intensities of components of the split reflexions indicates that the rhombohedral angle becomes less than the 60° required for cubic symmetry. This type of structure change is analogous to that found in the monoxides of iron, nickel and manganese (Rooksby & Tombs, 1951). No departure from cubic symmetry is evident in powder photographs of Fe_3O_4 at 165° K., so that the deformation of the structure occurs between 165 and 95° K.

Closely similar effects were obtained using a specimen of natural magnetite.

The crystal-structure data calculated from the X-ray patterns for Fe_3O_4 at 295, 165 and 95° K. are shown in Table 1.

It is noteworthy that the structure cell shows only very small changes in volume below room temperature.

The failure of others to observe the structure transition decisively may be partly due to the use of unsuitable material. Residual lattice strain, very small crystal size, or lack of homogeneity may produce sufficient line-broadening to mask the splitting of the powder reflexions, especially if other experimental conditions are unfavourable. Alternatively, with very small crystallites or in the presence of lattice strain it is possible that the structure transition may be suppressed over the temperature range investigated.

Discussion

It now seems that the structure transition in magnetite at low temperature is associated, like the specific-heat anomaly, with an antiparallel orientation of the spins of the magnetic atoms. Such an arrangement facilitates the development of the condition generally referred to as antiferromagnetism, and in terms of this condition the so-called lower Curie temperature has been explained by Néel (1948, 1950).

In the structure cell of magnetite the iron atoms, whether at fourfold or sixfold co-ordination positions, may be regarded as arranged in sheets perpendicular to the [111] direction. There is then an analogy with the arrangement of magnetic atoms in substances such as manganous oxide and ferrous oxide. In these oxides an antiferromagnetic condition has been postulated in which the spins of the magnetic atoms in a given (111) plane are parallel, but the spins in successive planes are antiparallel. If a similar antiparallel orientation of neighbouring (111) planes of magnetic atoms holds for magnetite, a deformation of the structure cell may well be expected by expansion or contraction along a direction perpendicular to these planes, i.e. along [111]. This is exactly the observed form of the structure transition in magnetite at low temperature.

Fe_3O_4 is thus added to the growing list of substances for which structure transitions have been observed in association with the development of antiferromagnetism (Rooksby & Tombs, 1951; Smart & Greenwald, 1951). Other spinels containing magnetic atoms are being studied.

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The crystal structures of some α-amino acids. A preliminary X-ray examination.

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As part of the work of this laboratory on the structure of proteins, the crystal structures of the α-amino acids and simple peptides are being studied. The results here recorded are for compounds representative of amino acids with straight (I) and branched (Ia) aliphatic chains, dicarboxylic (II) and heterocyclic (III) amino acids. The crystal structures of glycine (Albrecht & Corey, 1939) and of alanine (Levy & Corey, 1941; Donohue, 1950) have been studied in detail. The analysis of the copper salt and DL-α-aminobutyric acid (Stosick, 1945) has been completed for one projection only. The cell dimensions and space groups of DL-valine, DL-norleucine and DL-methionine have been recorded by Albrecht, Schnackenberg, Dunn & McCullough (1943), but their data have been proved unreliable by the present work and by the recent study of threonine (Shoemaker, Donohue, Schomaker &

Corey, 1950). Cell dimensions and space group of DL-leucine have been recorded by Möller (1949), and of L-aspartic and L-glutamic acids by Bernal (1931). A preliminary examination of L-proline has also been reported (Wright & Cole, 1949).

The cell dimensions, measured and calculated densities, number of molecules per unit cell (Z) and space group of the compounds investigated are given in Table 1, Möller's data for DL-leucine being added for completeness. The diffraction data were derived from rotation films and zero- and n-layer moving films taken on an equi-inclination Weissenberg goniometer (Mathieson, 1951).

The straight chain amino acids (I) crystallize in the monoclinic system, the space group being either $P2_1/a$ or $I2/a$. The occurrence of DL-α-amino-n-butyric acid with space group $P2_1/a$, DL-norvaline with $I2/a$ and DL-methionine in both forms suggests that all these compounds could display dimorphism under suitable conditions of crystallization. The form with space group $P2_1/a$ is referred to as α, that with $I2/a$ as β. From the detailed analyses of α- and β-DL-methionine and DL-norleucine, it was found that the crystal structure of these compounds is based on a double-layer unit, stacked along the c axis, the aliphatic chain lying approximately parallel to this axis. The molecules are linked by hydrogen bonds between nitrogen (of NH_3^+) and oxygen (of COO^-) atoms of adjacent molecules, the hydrogen bonds being distributed in an almost tetrahedral arrangement around the nitrogen atom. The weak van der Waals forces between the end methyl groups permit easy cleavage parallel to (001) and allow packing in two possible modes, as found for methionine. Combination of these two packing arrangements explains the occurrence of disorder in these compounds. Furthermore, for norleucine, the coexistence of these two types of packing in an ordered manner leads to a complex structure, with a c axis of 66·24 A. Order is not quite complete as is shown by spread of reflexions parallel to c^*.

The branched-chain acids (Ia) crystallize in the triclinic system, the space group being $P1$ or possibly $P\bar{1}$. From piezo-electric measurements on DL-leucine, Möller (1949) suggested that the space group is $P1$. Albrecht reported DL-valine as monoclinic, with space group $P2_1$ and cell dimensions $a=5{\cdot}20$, $b=22{\cdot}12$, $c=5{\cdot}41$ A., $\beta=109° 2'$. Diffraction data from our specimen of this compound gave no indication of monoclinic symmetry. The crystal structure is based also on a double-layer unit stacking parallel to c, but no evidence was obtained for the existence of the two forms necessary to account for the disorder in stacking mentioned by Möller.

The structure analyses of the two amino dicarboxylic acids have been carried out using their hydrohalides. For DL-glutamic acid, it was necessary to use both the hydrochloride and the hydrobromide, since the halogen atoms lie very close to a symmetry axis and do not fix the majority of phase angles.

The structure of the proline molecule has been determined by an analysis of the copper salt. The heavy copper atoms, at centres of symmetry, determine 50% of phase angles in the projections considered, namely, ($hk0$) and ($0kl$). The structure is based on octahedral bond formation around the copper atom, two proline molecules being bonded by nitrogen and oxygen in a square coplanar arrangement with a water molecule above and below the plane.

The dihydrochloride of tryptophane has been shown to be triclinic with two molecules in the unit cell. The presence of the chlorine atoms permits a reasonably direct approach to the structure analysis, which is in progress.

Detailed analyses of certain of these compounds will be given at a later date.

Our thanks are due to N. Stephenson, of the University of Sydney, and to H. Welsh for assistance in the determination of the data for tryptophane dihydrochloride and copper proline dihydrate respectively.

Table 1. *Crystallographic data*

Compound	a (A.)	b (A.)	c (A.)	α (°)	β (°)	γ (°)	Density (g.cm.$^{-3}$) Obs.	Density (g.cm.$^{-3}$) Calc.	Z	Space group
I										
α-DL-Amino-n-butyric acid	9·87	4·80	12·10	—	101	—	1·22	1·22	4	$P2_1/a$
β-DL-Norvaline	9·93	4·78	30·04	—	100	—	1·11	1·11	8	$I2/a$
α-DL-Norleucine	9·84	4·74	16·56	—	104·5	—	1·17	1·16	4	$P2_1/a$
-DL-Norleucine	9·84	4·74	66·24	—	104·5	—	1·17	1·16	16	—
α-DL-Methionine	9·76	4·70	16·70	—	102	—	1·34	1·33	4	$P2_1/a$
β-DL-Methionine	9·94	4·70	33·40	—	106·6	—	1·34	1·33	8	$I2/a$
Ia										
DL-Valine	5·25	5·43	11·05	91	92·4	109·4	1·315	1·31	2	$P1$ or $P\bar{1}$
DL-Isoleucine	5·30	5·36	13·16	96·1	89·9	108·9	1·24	1·24	2	$P1$ or $P\bar{1}$
DL-Leucine	5·18	5·39	14·6	96	103	111·5	1·18	—	2	$P1$
II										
DL-Aspartic acid	9·15	7·5	15·8	—	96	—	1·66	1·64	8	Ia or $I2/a$
DL-Aspartic acid hydrochloride hemihydrate	9·95	6·42	13·05	—	120	—	1·64	1·64	4	$P2_1/c$
DL-Glutamic acid hydrochloride	5·05	12·00	13·35	—	—	—	1·52	1·51	4	$P2_12_12_1$
DL-Glutamic acid hydrobromide	5·30	11·90	13·65	—	—	—	1·77	1·76	4	$P2_12_12_1$
III										
Copper/DL-proline dihydrate	5·62	17·85	7·13	—	106·5	—	1·61	1·59	2	$P2_1/n$
DL-Tryptophane dihydrochloride	5·30	8·61	16·20	103	107	98	1·38	1·37	2	$P1$ or $P\bar{1}$

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Thermal expansion coefficients of α-monoclinic selenium.

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Selenium crystals with particle size ranging from that of a fine powder to specimens approximately 1 mm. in their greatest dimension were obtained from a saturated solution of carbon disulfide. The samples examined showed no characteristics either to optical or X-ray examination to differentiate them into more than one class, Se_α.

The camera used was an adaptation of Buerger's (1937) precision back-reflection Weissenberg camera, diameter 7·993 cm., $K = 2°$ per mm., oscillation amplitude about 50°. The temperature was controlled by means of an electrically powered furnace designed by the author as a modification of the Buerger (1943) high-temperature powder camera. The single selenium crystal was mounted on the end of a short glass capillary and aligned on a goniometer head by means of Laue, rotation and Weissenberg photographs. It was then coated with fine filings of very pure aluminum, and the two desired Weissenberg patterns, one at tap-water temperature and the other at approximately 1 W. power input ($\Delta t \doteqdot 55°$ C.) were taken together on the same film.

The patterns were measured on a Cenco 10 cm. comparator. The aluminum powder lines, with the aid of the data of Nix & MacNair (1941), served, with known data on the aluminum thermal expansion and the measured tap-water temperature, to calibrate the film as to angle per millimeter and to give the value of the elevated temperature. Radiation used was unfiltered Cr for the 0,0,10 order and Co for all other cases. Exposure time was usually 5 hr. for each temperature run.

The breadth of the Se lines was less than 8′, the aluminum about 5′. Precision in the spacing values was about one part in ten thousand. The results are summarized in Tables 1 and 2.

Table 1. *Observations at particular temperatures*

Unit	t_1 (° C.)		t_2 (° C.)		Order indices
$a_0 \sin\beta$	20·0	9·0440 kX.	77·3	9·0427 kX.	860 and 680
b_0	20·0	9·0545	77·3	9·1003	860 and 680
	20·5	9·0546	75·2	9·0954	0,10,0
$c_0 \sin\beta$	21·0	11·573	80·2	11·615	0,0,10
β	24·2	90·882°	79·9	90·904°	709
	24·2	90·831	79·9	90·876	5,0,11

Table 2. *Summary at* 20° C.

Unit	Coefficient of expansion (per ° C.)	Author's values	Burbank's (1951) values	Klug's (1934) values
a_0	$-\ 1{\cdot}5 \times 10^{-6}$	9·046 kX.	9·05 kX.	8·992 kX.
b_0	$+84{\cdot}7 \times 10^{-6}$	9·054	9·07	8·973
c_0	$+63{\cdot}3 \times 10^{-6}$	11·573	11·61	11·52
β	$+\ 5{\cdot}5 \times 10^{-6}$	90° 52′	90° 46′	91° 34′
V	$+145 \times 10^{-6}$	947·7 kX.^{3}		

Author's values of a_0, b_0 and c_0 are ±0·001 kX. units; β is about ±3′.

In addition to the planes actually used to obtain the above, corroborative readings were made on the following neighboring planes, hot and cold: 1,10,0; 10,1,0 (not resolved since $\Delta\theta = 3'$ only); and 0,1,10.

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Spherical Patterson sections.

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Introduction

The lengths of certain interatomic, and particularly intraionic, vectors in an inorganic structure can often be predicted quite accurately from tables of atomic radii. In three-dimensional Patterson space peaks due to intraionic vectors can be identified at once if there is only one kind of complex ion; in a sulphate all the S–O peaks will be found on a sphere of radius 1·6 A. round the origin.