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Order Versus Disorder in Ternary Structures Including Certain Spinels¹

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The doubling process as the second alternative suggested by Professor M. v. Laue for mix-crystals is followed through in the case of lithium ferrite and it is shown in that case that all superlattice lines disappear when the lattice edge is eight times as large as the small disordered lattice found by Posnjak and Barth. It is shown that for this large (33A) lattice the *simple* space group, O_1^A , gives only face-centered lines on the powder photograph. The disappearance of the superlattice lines for this lattice may be said to be due to the coherence of the x-rays that cause the destructive interference involved.

1. INTRODUCTION

PROFESSOR W. L. Bragg in his Bakerian lecture, June 28, 1934, in conjunction with Dr. E. J. Williams,² discusses order *versus* disorder in alloys, and they call attention to some of the earlier work of others in this field. In general the effect of increasing temperature on alloys is to change an ordered lattice into a disordered one, and one may expect a sharp discontinuity in the specific heat of an alloy at the critical temperature as the temperature is lowered across it. With further lowering of the temperature the change in specific heat is more gradual as the degree of order is increased.

In his paper on the "Statistical Theory of Superlattices" Professor H. A. Bethe³ extended Bragg and Williams' definition of order so as to include local order; thus he defines long range and short range order, and calculates these for the simple cubic lattice; but interaction between nearest neighbors is alone considered. Chang⁴ has extended Bethe's theory to include interaction between next nearest neighbors and gets a better agreement with experiment.⁵ He shows that with increasing interaction between second neighbors, the value of the specific heat at the critical temperature is very sensitive to the exact

value chosen for this second neighbor interaction. He states, however, that it is not expected that his treatment should agree with experiment too well, for it leaves the higher interactions and the heat motions out of account. More recently Kirkwood⁶ has presented "an alternative theory of order and disorder, essentially equivalent to Bethe's in its degree of approximation." Bethe in a later paper⁷ adopts the method of Kirkwood.

Order-disorder problems in ternary alloys, or crystal structures, have, so far as the author is aware, received very little attention in the literature. In studying Posnjak and Barth's⁸ so-called principle of "variate atom equipoints" the writer was aware of the two points of view concerning "mix-crystals" discussed by M. von Laue⁹ in explanation of the results of Vegard and Schjelderup¹⁰ for some mix-crystals of alkali halides. The two views are these. In a mix-crystal the two components, *A* and *B* say, are either distributed statistically (in a disordered fashion) or else there is perfect order, but the lattice is *much* larger. Vegard and Schjelderup chose the first alternative. It is well known that certain of the alkali halides form solid solutions in all proportions.¹¹ These alkali halide mix-crystals are ternary, not binary, structures, yet with regard to mixing they are binary. In KBr-KCl there is a common cation, K. In KI-NH₄I there is a common anion, I. Both of these mixes form solid solutions in all proportions.¹¹

¹ Read before the American Physical Society, Indianapolis, Dec. 1937.

² Bragg and Williams, Proc. Roy. Soc. **A145**, 699 (1934). See also their second and third papers, Proc. Roy. Soc. **A151**, 540 and **A152**, 231 (1935). Many more references to earlier work are to be found in their second paper; the third paper is by Williams alone.

³ Bethe, Proc. Roy. Soc. **A150**, 552 (1935).

⁴ Chang, Proc. Roy. Soc. **A161**, 546 (1937); see also Bethe, J. App. Phys. **9**, 244 (1938).

⁵ Sykes, Proc. Roy. Soc. **A148**, 443 (1935).

⁶ Kirkwood, J. Chem. Phys. **6**, 70 (1938).

⁷ Bethe, J. App. Phys. **9**, 244 (1938).

⁸ Posnjak and Barth, Phys. Rev. **38**, 2234 (1931).

⁹ Laue, Ann. d. Physik **56**, 497 (1918).

¹⁰ Vegard and Schjelderup, Physik. Zeits. **18**, 93 (1917).

¹¹ E. g. Havighurst, Mack and Blake, J. Am. Chem. Soc. **47**, 29 (1925).

2. SUPERSTRUCTURES

In binary alloys, when the degree of order is high, there is in general a tendency for superlattice lines to appear, because of the two superstructures present. The difference in scattering power for x-rays of the two components present results in extra reflections that are not present when the disorder is complete. This is well illustrated in the copper-gold alloy, Cu_3Au , studied by Sykes and Evans.¹² For a copper-gold wire heated to 425°C and quenched in water, only eight face-centered lines appeared on the powder photograph. After ordering by various methods of cooling, twelve extra superlattice lines appear, all of which are simple cubic. Techniques were developed by them for changing the character of the superlattice lines from fuzzy to sharp.

3. SECOND ALTERNATIVE FOR MIXED CRYSTALS

Since M. v. Laue⁹ derived his expression for the structure factor of the mix-crystal K_2BrCl , most people have chosen the first (disordered) alternative in studying binary or ternary alloys, or structures, for oftentimes superlattice lines are absent, and such lines are at once eliminated by assuming disorder. Where possible, it is much more scientific to study specific heats of structures as a function of temperature, as well as to make an x-ray analysis of the structures. But superlattice lines can be eliminated by the second alternative, *viz.*, that of choosing a larger lattice. When properly done, it is possible, in some cases at least, to obtain the exact equivalent of the

disordered lattice; and even though crystallographers and metallurgists might say that this large equivalent of the small disordered lattice could never be produced owing to an infinite time being needed for its formation, it is worthy of having attention called to it.

4. LOW TEMPERATURE MODIFICATION OF LITHIUM FERRITE

A couple of years ago I secured from Dr. Barth of the Geophysical Laboratory some of the powdered lithium ferrite and zinc stannate that he and Dr. Posnjak had used in their spinel studies¹³ and that led them to announce their principle of "variate atom equipoints." Powder photographs of these two compounds were taken with molybdenum $K\alpha$ -rays, and the photographs were densitometered. Proper¹⁴ account was taken of all of the intensity factors and of the laws of photographic blackening for x-rays. The results for lithium ferrite are shown in Table I, together with the observed results of Barth and Posnjak. The chief differences between my results and theirs is due to their overestimation of the intensity for faces having large values of θ for fairly long times of exposure. When the exposure time is long (i.e., $S > 0.6$ for the strongest line on the film) there is an exhaustion of silver for lines having θ small as against those having θ large, thus leading to errors.

In studying this second alternative a frontal attack was made on the problem by doubling the lithium ferrite lattice from 4.141Å to 8.282Å, care being used to increase the symmetry of the crystal if possible as the size was doubled. It is always possible in a crystal lattice to move the origin of coordinates without affecting intensity relations, though symmetry properties are thereby affected. In all cases I have chosen an oxygen atom as origin. Allowing no exchange between iron and lithium atoms, one is, of course, conscious in the 8.28Å cell that neighboring 4.14Å parts are not identical. Indeed, if one alternates lithium and iron in between the oxygen atoms in all directions parallel to the axes, he is conscious that when he has progressed along the

TABLE I.*

hkl FOR 4.14Å LAT- TICE	OBSERVED INTENSITIES		CALCULATED INTENSITIES (33Å LATTICE)					
	POSNJAK AND BARTH	BLAKE	$n\phi \Sigma SF ^2$		$n\phi \Sigma SF e^{-M} ^2$		$n\phi \Sigma SF e^{-M} ^2 \Delta$	
			IONIC	ATOMIC	IONIC	ATOMIC	IONIC	ATOMIC
111	40	27	15.3	22.1	15.5	23.5	15.5	23.4
200	100	100	100.0	100.0	100.0	100.0	100.0	100.0
220	90	60	58.5	61.0	55.7	58.1	56.0	58.5
311	30	12	10.3	12.5	10.6	12.8	10.7	12.9
222	40	18	18.1	19.3	16.5	18.5	16.7	18.7
400	20	6	7.7	8.2	6.7	7.2	6.8	7.3
331	10	5	4.5	5.5	4.5	5.5	4.6	5.6
420	50	14	19.9	20.4	16.7	17.2	17.0	17.5
422	40	9	13.6	14.3	11.0	11.6	11.3	11.9

* For an explanation of the symbols appearing in the intensity formulas see Blake, Rev. Mod. Phys. 5, 169 (1933); also J. Chem Phys. 2, 320 (1934).

¹² Sykes and Evans, J. Inst. Metals 58, 255 (1936).

¹³ (a) Barth and Posnjak, J. Wash. Acad. Sci. 21, 255 (1931); (b) Posnjak and Barth, Phys. Rev. 38, 2234 (1931); (c) Zeits. f. Krist. 82, 325 (1932).

¹⁴ Blake, Rev. Mod. Phys. 5, 169 (1933).

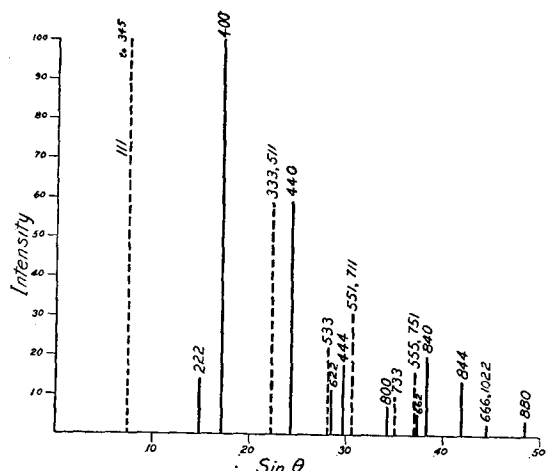


FIG. 1. Calculated intensities for 8.28Å lattice.

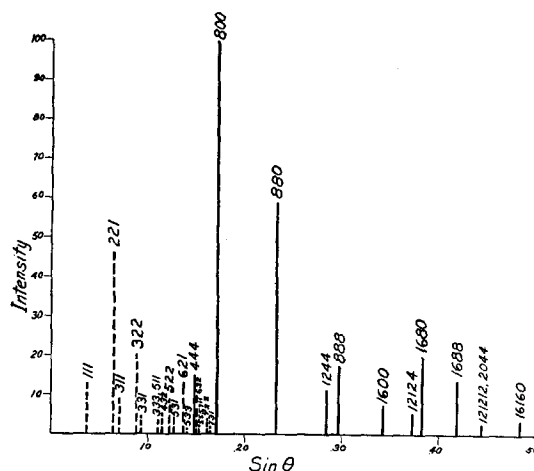


FIG. 2. Calculated intensities for 16.56Å lattice.

cubical axes 8.28Å the structure he has thus built up is only a piece of a cell, for at one corner he finds an oxygen atom with three iron atoms as nearest neighbors while at the opposite corner (that furthest removed) an oxygen atom is surrounded by three lithium atoms as nearest neighbors, the oxygen atoms at the other four corners having two lithium and one iron as nearest neighbors, or *vice versa*. Thus this 8.28Å lattice is only one-eighth of a proper unit cell, and it is not surprising that when one plots intensity calculations against $\sin \theta$ he gets a great overstressing of the superlattice (dotted) lines (faces), the full lines in Fig. 1 being the calculated face-centered lines that are observed, where for the calculations all intensity factors are taken into account except the temperature factor and the absorption factor. The *first legitimate* doubling of the lattice enlarges it at once to 16.56Å. For, by inserting axial planes of symmetry, each oxygen atom at the corners of the enlarged lattice is surrounded by three iron atoms as nearest neighbors, while the oxygen atom at the center is surrounded by six lithium atoms as nearest neighbors. This fact determines the space-group of the lattice, *viz.*, simple cubic O^1_h . When the intensity relations are calculated and plotted (Fig. 2), it is noticed that the superlattice (dotted) lines are reduced in intensity, being largely crowded down into the region where θ is small. But since the powder photographs show their absence, another lattice doubling (the

second legitimate one) is suggested. Thus the correct, *ordered* lattice, that is, the *exact* equivalent of the statistical averaging of Posnjak and Barth's 4.141Å lithium ferrite lattice, has eight times the edge of that lattice, *viz.*, 33.13Å. The result is shown in Fig. 3. The only superlattice line residue is for face 333, and it has an intensity less than 4 percent and hence could not be detected, for it occurs in the region of maximum general blackening. Moreover in Posnjak and Barth's observations no line is reported whose intensity is less than ten percent. In what I call the second legitimate doubling it should be borne in mind that care was used to preserve the axial planes of symmetry. This second doubling again gives the space-group as O^1_h . Thus an

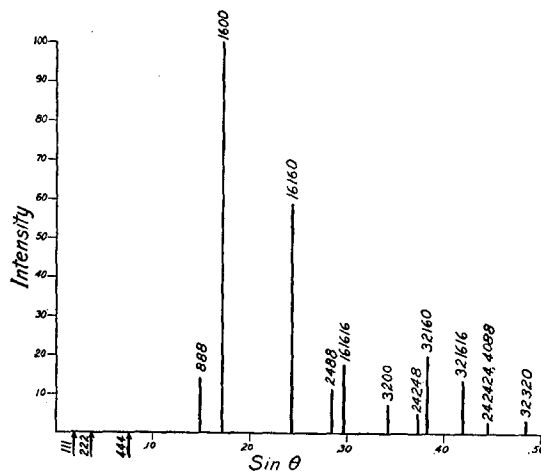


FIG. 3. Calculated intensities for 33.13Å lattice.

TABLE II. *Coordinates of oxygen atoms.*

$\begin{smallmatrix} x \\ z \end{smallmatrix}$	0	1	2	3	4	5	6	7	$\bar{8}$	$\bar{7}$	$\bar{6}$	$\bar{5}$	$\bar{4}$	$\bar{3}$	$\bar{2}$	$\bar{1}$	0	$\begin{smallmatrix} x \\ z \end{smallmatrix}$
0	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	0
1	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	1
2	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	2
3	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	3
4	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	4
5	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	5
6	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	6
7	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	7
$\bar{8}$	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	$\bar{8}$
$\bar{7}$	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	$\bar{7}$
$\bar{6}$	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	$\bar{6}$
$\bar{5}$	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	$\bar{5}$
$\bar{4}$	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	$\bar{4}$
$\bar{3}$	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	$\bar{3}$
$\bar{2}$	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	$\bar{2}$
$\bar{1}$	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	$\bar{1}$
0	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	0
$\begin{smallmatrix} z \\ x \end{smallmatrix}$	0	1	2	3	4	5	6	7	$\bar{8}$	$\bar{7}$	$\bar{6}$	$\bar{5}$	$\bar{4}$	$\bar{3}$	$\bar{2}$	$\bar{1}$	0	$\begin{smallmatrix} z \\ x \end{smallmatrix}$

TABLE III. *Coordinates of iron atoms.*

$\begin{smallmatrix} x \\ z \end{smallmatrix}$	0	1	2	3	4	5	6	7	$\bar{8}$	$\bar{7}$	$\bar{6}$	$\bar{5}$	$\bar{4}$	$\bar{3}$	$\bar{2}$	$\bar{1}$	0	$\begin{smallmatrix} x \\ z \end{smallmatrix}$
0	1	0	3	2	1	0	3	2	1	2	3	0	1	2	3	0	1	0
1	0	3	2	1	0	3	2	1	0	1	2	3	0	1	2	3	0	1
2	3	2	1	0	3	2	1	0	3	0	1	2	3	0	1	2	3	2
3	2	1	0	3	2	1	0	3	2	3	0	1	2	3	0	1	2	3
4	1	0	3	2	1	0	3	2	1	2	3	0	1	2	3	0	1	4
5	0	3	2	1	0	3	2	1	0	1	2	3	0	1	2	3	0	5
6	3	2	1	0	3	2	1	0	3	0	1	2	3	0	1	2	3	6
7	2	1	0	3	2	1	0	3	2	3	0	1	2	3	0	1	2	7
$\bar{8}$	1	0	3	2	1	0	3	2	1	2	3	0	1	2	3	0	1	$\bar{8}$
$\bar{7}$	2	1	0	3	2	1	0	3	2	3	0	1	2	3	0	1	2	$\bar{7}$
$\bar{6}$	3	2	1	0	3	2	1	0	3	0	1	2	3	0	1	2	3	$\bar{6}$
$\bar{5}$	0	3	2	1	0	3	2	1	0	1	2	3	0	1	2	3	0	$\bar{5}$
$\bar{4}$	1	0	3	2	1	0	3	2	1	2	3	0	1	2	3	0	1	$\bar{4}$
$\bar{3}$	2	1	0	3	2	1	0	3	2	3	0	1	2	3	0	1	2	$\bar{3}$
$\bar{2}$	3	2	1	0	3	2	1	0	3	0	1	2	3	0	1	2	3	$\bar{2}$
$\bar{1}$	0	3	2	1	0	3	2	1	0	1	2	3	0	1	2	3	0	$\bar{1}$
0	1	0	3	2	1	0	3	2	1	2	3	0	1	2	3	0	1	0
$\begin{smallmatrix} z \\ x \end{smallmatrix}$	0	1	2	3	4	5	6	7	$\bar{8}$	$\bar{7}$	$\bar{6}$	$\bar{5}$	$\bar{4}$	$\bar{3}$	$\bar{2}$	$\bar{1}$	0	$\begin{smallmatrix} z \\ x \end{smallmatrix}$

ordered simple cubic lattice, of edge 33.13Å, containing 512 molecules of $\text{Li}_2\text{Fe}_2\text{O}_4$, with cations differing in scattering power as 23 to 2 (or as 26 to 3 if neutral atoms) gives only face-centered reflection intensities. I invite the attention of the crystallographers to this fact. I think this gives the answer also to the question implied in this sentence of Posnjak and Barth's paper on lithium ferrite, "Taking into consideration not too small a portion of the crystal, an equal number of points is occupied by iron and by lithium." The "not too small a portion" is a cube of 33Å edge.

In order that others who care to may study this 33Å lattice for themselves, I give in Tables II, III and IV the atomic positions of the oxygen, iron and lithium atoms, respectively, with certain necessary explanations. In Table II the figures 0 and 1 occur while in Tables III and IV the figures 0, 1, 2, 3 occur. Let any figure in any of the three tables represent the numerator of a fraction of which the denominator is 16. To illustrate, choose the figure 3, then 3/16 is the y coordinate of an atom whose x and z coordinates are given (also as numerators of fractions having the denominator 16) at the top and side of each

table, where it is understood that $\bar{7}/16$ is the same as $9/16$, because the unit angle chosen for the revolving radius vector¹⁵ is $2\pi/16 = 22.5$ degrees. Thus the least count in stating the exact position of an atom along any of the three axes is 1/16 of the lattice edge. One interprets the tables correctly thus.

Since there are 16 units along the x and z axes, there must be 16 units along the y axis. In Table II only two such units are given by the figures 0 and 1 as numerators of y for positions occupied by 256 oxygen atoms. To obtain positions of another 256 of the total 2048 oxygen atoms in the unit cell, it is necessary to substitute 2 for 0, and 3 for 1, in the y values of Table II. Similar substitutions of 4, 6, $\bar{8}$, $\bar{6}$, $\bar{4}$, and $\bar{2}$ for 0, and of 5, 7, $\bar{7}$, $\bar{5}$, $\bar{3}$, and $\bar{1}$, for 1, give the coordinates of the remaining oxygen atoms. Table III gives the coordinates of 256 iron atoms. The remaining iron atom positions, which total 1024 in the unit cell, are obtained by substitutions of 4, $\bar{8}$, and $\bar{4}$ for 0, of 5, $\bar{5}$, and $\bar{1}$ for 1, of 6, $\bar{6}$, and $\bar{2}$ for 2, and of 7, $\bar{7}$ and $\bar{3}$ for 3, in the y values of Table III. The same substitutions made in Table IV

¹⁵ See Blake, J. Chem. Phys. 2, 320 (1934).

TABLE IV. *Coordinates of lithium atoms.*

$\begin{smallmatrix} x \\ z \end{smallmatrix}$	0	1	2	3	4	5	6	7	8	7	6	5	4	3	2	1	0	$\begin{smallmatrix} x \\ z \end{smallmatrix}$
0	3	2	1	0	3	2	1	0	3	0	1	2	3	0	1	2	3	0
1	2	1	0	3	2	1	0	3	2	3	0	1	2	3	0	1	2	1
2	1	0	3	2	1	0	3	2	1	2	3	0	1	2	3	0	1	2
3	0	3	2	1	0	3	2	1	0	1	2	3	0	1	2	3	0	3
4	3	2	1	0	3	2	1	0	3	0	1	2	3	0	1	2	3	4
5	2	1	0	3	2	1	0	3	2	3	0	1	2	3	0	1	2	5
6	1	0	3	2	1	0	3	2	1	2	3	0	1	2	3	0	1	6
7	0	3	2	1	0	3	2	1	0	1	2	3	0	1	2	3	0	7
8	3	2	1	0	3	2	1	0	3	0	1	2	3	0	1	2	3	8
7	0	3	2	1	0	3	2	1	0	1	2	3	0	1	2	3	0	7
6	1	0	3	2	1	0	3	2	1	2	3	0	1	2	3	0	1	6
5	2	1	0	3	2	1	0	3	2	3	0	1	2	3	0	1	2	5
4	3	2	1	0	3	2	1	0	3	0	1	2	3	0	1	2	3	4
3	0	3	2	1	0	3	2	1	0	1	2	3	0	1	2	3	0	3
2	1	0	3	2	1	0	3	2	1	2	3	0	1	2	3	0	1	2
1	2	1	0	3	2	1	0	3	2	3	0	1	2	3	0	1	2	1
0	3	2	1	0	3	2	1	0	3	0	1	2	3	0	1	2	3	0
$\begin{smallmatrix} z \\ x \end{smallmatrix}$	0	1	2	3	4	5	6	7	8	7	6	5	4	3	2	1	0	$\begin{smallmatrix} z \\ x \end{smallmatrix}$

obviously give the positions of the 1024 lithium atoms in the unit cell. To obtain the positions of all atoms in any one plane of the unit cell, e.g. $y=1/16$, take the positions of the figures 1 in Table II as the positions of oxygen atoms in the plane $y=1/16$, the positions of figures 1 in Table III as the positions of iron atoms in that plane, and the positions of the figures 1 in Table IV as the positions of lithium atoms in the same plane.

A few words as to the space group, O_h or $Pm3m$. In calculating the structure factor the general formulas give $A = \sum \cos 2\pi hx [\cos 2\pi ky \cdot \cos 2\pi lz + \cos 2\pi ly \cdot \cos 2\pi kz]$, and $B=0$. But I have found it no easier to use these formulas than to summarize by the revolving vector method.¹⁵ As already stated, assuming that for the spinels the absorption and temperature factors pretty well cancel each other, the correct intensity relations are given in Fig. 3 and these agree well enough with the lithium ferrite observations of Table I. The atomic form factors for lithium, iron and oxygen used are those of the *International Tables for the Determination of Crystal Structures*, the crystal being taken as ionic or atomic as indicated in Table I.

In the case of zinc stannate, I have tried the doubling process on the 8.61Å disordered lattice given by Barth and Posnjak^{13c} to see if I could get the large lattice equivalent; but I haven't completed the study for the reason that if it is also true in this case that the lattice edge should be enlarged eight times, the labor involved becomes quite burdensome, for the cell would then have an edge 68.88Å. The 34.44Å cell containing 512 molecules of Zn_2SnO_4 goes to zero for the fourth order of 311, no matter what value is used for the oxygen parameter. This indicates another doubling, or some sort of reorganization of the cell. I intend to study the doubling process further in the case of zinc stannate.

5. LARGE-SIZED LATTICES AND MOLECULES

It is becoming more fashionable to speak of large-sized lattices, even if in some cases there is apparently but one molecule per unit cell. The recent series of papers in *Nature*,¹⁶ "Crystal Structure of the Proteins," gives a tetragonal lattice, $a=b=63.5\text{Å}$, $c=145\text{Å}$, and an orthorhombic lattice, $a=49.6\text{Å}$, $b=67.8\text{Å}$, $c=66.5\text{Å}$, Bernal, Fankuchen and Perutz stating that "the proteins fall into two groups, pseudo-hexagonal and pseudo-cubic, in both cases with a side of 60–75Å." Long needle-like structures up to a length of 6000Å seem to have been prepared by Astbury and Bell.¹⁷ What is the distinction in building blocks between the spinels and these organic compounds that would prevent 33Å cubes for the lithium ferrite? In Sykes and Evans' paper, "The Transformation in the Copper-Gold Alloy, Cu_3Au ,"¹² the authors conclude that when this alloy was cooled at 30°C per hour it consisted of small "nuclei" within the individual crystals; so they distinguish between two different states of the alloy, one with nuclei, the other without. Each nucleus could be said to have 100 percent local order but an aggregation of nuclei could lack long range order. It seems to me that the 33Å lithium ferrite lattice discussed in this paper shows 100 percent local order and 100 percent long range order, that is, the nuclei are properly fitted together. A recent remark of Professor H.

¹⁶ Crowfoot and Riley; Crowfoot and Fankuchen; Bernal, Fankuchen and Perutz; *Nature* **141**, 521–524 (1938).

¹⁷ Astbury and Bell, *Nature* **141**, 747 (1938).

A. Bethe to the writer, that there ought to be more than one way in which all superlattice lines could be eliminated for a lattice as large as 33Å, leads me to admit the possibility, but not the probability, of this unless the local order is in a nucleus as small as 4.14Å, when the long range disorder is 100 percent. It should be borne in mind that if one turns the 33Å lattice inside out, as it were, that means nothing but an interchange throughout the lattice of iron and lithium atoms, thus giving the same, not a different, solution.

Granted that this 33Å, ordered lithium ferrite, according to present notions concerning alloys, could not be produced in the laboratory because of the inordinate amount of time required to set it up, it nevertheless remains as the low temperature form of the disordered 4.14Å lattice of lithium ferrite. Further studies on rates of cooling of alloys with specific heat measurements and with the possible use of "stabilizing agents" may

help to clarify the knotty problems involved in *order versus disorder* studies. Bragg and Williams² in their first study in this field remark as their concluding sentence, "Maxima and minima in physical properties at certain relative proportions (e.g. Fe₃Al and Cu₃Au) are statistical effects, and do not imply the existence of corresponding compounds." It seems conceivable to the writer that an ordered solution of such binary alloys could be found, in which case it would be a fair question to ask whether a single ordered-lattice alloy is not a definite compound. It has been shown that proper ordering causes superlattice lines to disappear, that a large (33Å) lattice of lithium ferrite is the exact equivalent of the small (4.14Å) disordered lattice, that a simple cubic lattice of edge 8 times the disordered face-centered cubic lattice gives only face-centered lines on the powder photograph in the case of lithium ferrite.

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The Dipole Moments of Molecules Containing Two Movable Dipoles

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The average dipole moment of a molecule containing two movable dipoles has been calculated as a function of temperature and restriction to internal rotation for three different potential functions. The potential functions used are: $(V_0/2)(\cos \phi + 1)$, $(V_0/\pi)(\pi - \phi)$ and $V_0/\pi^2(\pi - \phi)^2$, where V_0 is the difference in potential energy between the *cis* and *trans* forms of the molecule and ϕ is the angle between the planes containing the dipoles and the axis of rotation. Values of the integral $\int_0^\pi \cos x \exp(-bx^2)dx$ are tabulated for values of b ranging from 0 to 2 at intervals of 0.1. The dipole moments of *s*-dichloro-ethane, 1,2-bromo-chloro-ethane and *s*-dibromo-ethane as a function of temperature are used with the three potential functions to determine values of V_0 . The values thus obtained are compared with the values obtained by other methods.

INTRODUCTION

THERE have recently been several attempts to determine the magnitude of the potential barrier restricting internal rotation around single carbon-carbon bonds. Most of these attempts have been made on ethane.¹ In attacking

the problem from the standpoint of dipole moments it is necessary to substitute for symmetrically located hydrogen atoms, polar groups whose relative orientations will have a large effect on the resultant dipole moment of the molecule. In order to treat successfully the dipole moment data of such molecules as the 1,2-disubstituted ethanes it is necessary to derive expressions relating the observed dipole moment to the height and shape of the potential barrier and the individual bond moments. We have de-

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¹ Kemp and Pitzer, *J. Chem. Phys.* **4**, 749 (1936); *J. Am. Chem. Soc.* **59**, 276 (1937). Howard, *Phys. Rev.* **51**, 53 (1937). Kistiakowsky and Nazmi, *J. Chem. Phys.* **6**, 18 (1935). Bartholomé and Karweil, *Zeits. f. physik. Chemie* **39**, 1 (1938). Hunsman, *Zeits. f. physik. Chemie* **39**, 23 (1938).