their atoms seems necessary to account for their existence as stable groupings." These "directional forces," as appears from the preceding discussion by Wyckoff, are what he terms "valency bondings," so that it would appear that the X-ray study of crystal structure favors Zambonini's view, which implies control by valency, rather than Wherry's simpler, purely spatial one.

It would appear[8] that Barlow and Pope[9] were the first, or among the first, as far back as 1906, to suggest that isomorphism depended on the replacement of atoms of similar sizes, as well as on like valency.

STERRY HUNT AND THE THEORY OF THE PLAGIOCLASES

It may be of interest to American mineralogists to add that Zambonini, in another paper,[10] calls attention to the fact that Sterry Hunt[11] antedated Tschermak by about ten years in considering the members of the plagioclase group as mixtures of isomorphous albite and anorthite, and that the feldspars intermediate between the extremes are not definite mineral species.

ON STRUCTURE AND ISOMORPHISM IN CRYSTALS

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In a recent number of THE AMERICAN MINERALOGIST an interesting paper[1] has appeared which states that "It now seems probable that the principal requisite of isomorphous replaceability is that the elements in question must possess approximately identical volumes, at least in simple compounds, the crystal structures of which represent fairly close packing of the constituent atoms." An abstract[2] of a paper expressing similar ideas has also been published.

In the second paper[2,3] it is considered that isomorphous replacement will occur when there is a balancing of the valences of the atoms concerned and when at the same time the volumes of the

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[8] Cf. J. N. Friend, The Theory of Valency, 175–181, **1915.**

[9] Barlow and Pope, *Trans. Chem. Soc.*, **89,** 1724, 1906.

[10] F. Zambonini, *Rend. Accad. Lincei,* **31,** 341, (May 7), 1922.

[11] T. Sterry Hunt, *Am. J. Sci.*, **18,** 270, 1854; *Phil. Mag.*, **9,** 354, 1855. See also Hunt's Chemical and Geological Essays, 444, **1875.**

[1] E. T. Wherry, *Am. Mineralogist,* **8,** 1, 1923.

[2] F. Zambonini [H. S. Washington], *Am. Mineralogist,* **8,** 81, 1923.

[3] F. Zambonini, *Rend. Accad. Lincei,* **31,** 295, 1922.

replacing atoms are approximately equal to the volumes of those replaced. In the first article[1] the importance of the valence factor is rather minimized. Unfortunately, from the standpoint of the crystal analyst, the phenomena are not so simple as they thus appear.

To begin with it must be remarked that no general and exact statement of the connection between isomorphism and atomic arrangement can be made at the present time. In most cubic and in all other crystals the positions of atoms will not be fixed solely by symmetry properties. The few experiments yet made show that even in such simple isomorphous crystals as the carbonates of calcium and of manganese, the variable parameters defining the positions of some atoms will not have the same values. Thus it is seen that isomorphous crystals need not, and in general will not, have identical crystal structures. In fact the only field in which identity in the structures of two crystals will be more than an affair of chance is amongst the cubic crystals for which isomorphism itself has lost its usual significance. Because there is no equality between the structures of isomorphous crystals, and because isomorphism has a definite meaning in the field of crystallography itself, it seems more appropriate not to saddle upon it an indefinite crystal-structure import. To meet the need of describing crystals whose structures are sufficiently alike so that they will be crystallographically isomorphous, the term *homeotaxial*[4] will be employed. Two crystals are to be understood as homeotaxial when they are chemically alike with the same type of atomic arrangement and when the distributions of atoms are so nearly similar that they are isomorphous in the usual sense. Thus pyrite and hauerite are homeotaxial because they are similar chemically, and have the same type of cubic atomic arrangement even though the parameter defining the positions of the sulfur atoms is somewhat different in the two instances; but zinc blende and galena are not homeotaxial, even though they are chemically similar and are both cubic, because the type of atomic arrangement is different in the two. It will be noted that homeotaxial is more specialized in meaning than isomorphous because though all homeotaxial crystals are isomorphous in its widest sense, isomorphous crystals need not have the same sorts of atomic arrangement and consequently may not be homeotaxial. With the existing complete

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[4] The writer wishes to thank H. S. Washington for this term.

lack of knowledge of the atomic groupings in complicated crystals, it is impossible to set any definite limits to the variations of structure within which crystals will remain homeotaxial.

The substitution of an atom for one of a different element in the production of mixed crystals may either leave the mixed crystal homeotaxial with the original or may alter its form markedly. If the replacement is one of the first sort it is an isomorphous atomic replacement.

It would appear that the working basis of the first paper referred to above is contained in the statement that in crystals which are composed of atoms of approximately constant volumes packed closely together, substitution of one atom for another of a different kind without change in the crystallographic characteristics (the axial ratios and angles) can take place whenever the interchanged atoms have practically the same effective volumes.

This view of the nature of crystals is of the greatest antiquity, repeating itself with but slight variations from the time of the ancient philosophers to the present. Some 25 years ago it was developed at considerable length by Sollas,[5] who, however, did not look upon crystals as necessarily close-packed structures. Barlow and Pope[6] in adding their assumption correlating valency with volume made these atomic spheres close-packed. In its latest appearance as the hypothesis of constant atomic radii W. L. Bragg[7] stresses the constancy of the radius (and volume) of an atom from crystal to crystal. The information from crystal structure study using X-rays offers the chance of testing out these views. It must be said that the existing data do not accord with either close-packing or constant size[8] of atoms. In crystals that are homeotaxial there is an additivity of atomic dimensions which may, if desired, be expressed in terms of an hypothesis of constant atomic radii. Between other crystals not homeotaxial this additivity no longer holds, the variation from it apparently becoming greater the less alike are the structures of the crystals involved. Hence the atomic radii calculated from the various crystals which can serve as starting points may be quite different from one another. If the radius of the cadmium atom is calculated from metallic cadmium,

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[5] W. J. Sollas, *Proc. Roy. Soc. London*, **68**, 270, 1898, etc.

[6] Barlow and Pope, *Trans. Chem. Soc.*, **89**, 1724, 1906.

[7] W. L. Bragg, *Phil. Mag.*, (6) **40**, 169, 1920.

[8] R. W. G. Wyckoff, *Proc. Nat. Acad. Sci.*, **9**, 33, 1923.

the radius of oxygen obtained from this value for cadmium through cadmium oxide, and the size of other atoms reached by the simple extension of this process to other crystals, the resulting series of atomic dimensions would be somewhat different from those derived from the related metallic zinc, for instance. They would also differ from those deduced from the diamond as a starting point or from the series calculated through pyrite. In fact the results of all of these series that have been mentioned would be unlike. It is seen thereby that the hypothesis of truly constant atomic radii is experimentally disproved. Still the "radius" of a particular atom may not be expected to be enormously greater, meaning thereby several times greater by volume, in one crystal than in another. The point of importance to this discussion, however, lies in the fact that except possibly in some of the strongly electropositive and electronegative atoms the difference in size between various atoms may not be greater than the changes in dimensions of the same atom in passing from one sort of a crystal to another. By choosing for discussion examples of replacement which involve the alkali and alkaline earth metals, the most favorable cases have been considered, but the myriad of replacements which should be possible but are not found amongst the rest of the atoms in crystals under the explanation now being discussed have been ignored.

While this idea of constant atomic radii may perhaps be thought of as holding somewhat approximately, in the sense that the radius of one kind of atom probably does not change by multiples of its own size, the other part of the view, which regards crystals as closely packed structures, runs absolutely counter to the results of crystal analysis. Aside from the simple metals, the large majority of structures which have thus far been elucidated are more or less distended arrangements of atoms. Furthermore at the present time there is no information which might lead us to understand either why the atoms within a crystal do not closely pack together, or why, for compounds which seem closely related to one another, some will have one kind of an arrangement while others may be possessed of a totally different one. Examples of these differences in structure could be multiplied almost without limit. Thus the sodium chloride arrangement, which is itself not a very close-packed grouping of spheres, is a common one for the alkali halides and the oxides, sulfides, etc. of divalent metals. Yet its failure to be a universal one is clear from Table 1.

TABLE 1

NaCl grouping		**NH_4Cl grouping**	**Cubic ZnS grouping**	**ZnO grouping**
LiX	NaX	CsCl	CuCl	AgI
KX	RbX	CsBr	CuBr	CdS
CsF	NH_4I	CsI	CuI	ZnS
MgO	CaO	TlCl	ZnS	ZnO
CdO	AgCl	NH_4Cl		
NiO	AgBr	NH_4Br		
CaS	MnS			

NOTE: In this table X will represent any of the halogen atoms.

In the face of the overwhelming crystal structure evidence it is impossible either to make the assumption that crystals are closely packed or at the present time to prophesy anything about atomic arrangement in advance of experimental determinations.

Many data are at hand to show that neither homeotaxis nor isomorphism is determined primarily by the effective "sizes" of atoms. For example among the simple compounds, similar crystals of such widely different molecular volumes as lithium fluoride and caesium fluoride are completely homeotaxial, as are the more complicated potash and caesium alums; and iodine can be substituted for chlorine in the hexammonates of the nickel halides, for instance, without any alteration of atomic arrangement.

The possibility of solid solution between albite and anorthite is accounted for in the papers[1,2,3] under consideration by saying that the sum of the "volumes" of the replacing calcium and aluminum of the one crystal is equal to the sum of the replaced sodium and silicon of the other. If this criterion were the basic one it should be possible to effect a replacement of this sort in the cubic garnets, calcium and aluminum being replaced by sodium and more silicon. This should be true under the conclusions laid down in both of these papers, for not only would no change in volume take place but also there is a complete balancing of valences. As a matter of fact no cubic mixed garnets of this sort are found.

There probably can be no quarrel with the statement that isomorphous atomic replacements, or solid solution formation, will not take place unless the interatomic distances of the corresponding atoms involved in the substitutions are closely similar. This fact, which has long been known in the form of the rule of equal molecular volumes and is often emphasized, can of course be expressed in terms of "atomic radii," taking due recognition of the indefiniteness of these "atomic dimensions." The results of crystal analysis do not, however, justify that extension of this idea which finds in this equality of interatomic distances the primary cause and principal determining factor of isomorphous atomic replacements. In the absence of any real knowledge of the atomic arrangement in crystals with low symmetry, the precise nature of the other governing factors remains unknown as heretofore and no satisfactory explanation of such complex solid solutions as arise from albite and anorthite can be offered.

Nevertheless a somewhat more detailed discussion of the requirements of these mixed feldspars may throw some light upon the general character of other factors. In crystals of high symmetry experiment has shown that most, if not all, of the atoms of a given chemical kind have atoms of other sorts distributed about them in identically the same manner, that is they are *equivalent* to one another. In arrangements of less and less symmetry it is generally true that fewer and fewer of the chemically like atoms are equivalent. Thus, whatever the structure of the calcium aluminum garnet [$Ca_3Al_2Si_3O_{12}$] may be, it is quite certain that either all of the atoms of a sort are equivalent or that they fall into a few groups of equivalent atoms. In anorthite [$CaAl_2Si_2O_8$] the low degree of symmetry precludes the possibility of an equivalence of many of its atoms. This non-equivalence of the atoms in crystals of low symmetry, combined with the fact that most of them have positions not completely fixed by symmetry requirements, presents the possibility of building up many arrangements which are nearly but not exactly alike both in atomic grouping and in dimensions of the unit cells. It would appear that albite and anorthite are two such similar structures. How closely the positions of the sodium and silicon atoms of the one approach to the positions of the calcium and aluminum atoms of the other it is now impossible to say.

In the simple isomorphous replacement of but one kind of atom in a crystal, for instance in the formation of mixed crystals of KCl and KBr, the replacing bromine atoms, let us say, apparently can occupy any chlorine positions within the crystal and will be distributed in a haphazard fashion. A simple isomorphous mixing of barium in anorthite would not be expected for the same reason that sodium and rubidium chlorides do not mix, that is, because the unit cells probably differ too much in size, or because their molecular volumes are too unlike, or because the atomic "radius" of rubidium or of barium is too much greater than that of sodium or of calcium. Any of these "explanations" may be used for they all express the same idea. In such dual replacements as occur when albite and anorthite mix, where the replacing and replaced atoms are not chemically similar, the distribution must be more complex than in simple replacements. For if the inserted pair are not intimately associated together in place of those removed, the requirements of (electrical) stability of the structure will be disturbed in that small region. It consequently would seem necessary that these mixed feldspars should be constituted somewhat as if they were composed of an intimate mixing of albite and anorthite groupings of atoms. Geometrically it might be pictured much as if one unit cell had the albite arrangement while neighboring ones might be possessed of that of anorthite. Of course it must be borne in mind that this is only a diagrammatic representation, for in a real crystal some of the atoms of one unit cell will always be shared by those of neighboring cells. At the same time it may well be that the distribution in one part of a unit is that of albite and in the rest that of anorthite. The essential difference between this kind of a replacement and the simple one in which the entering atoms can go into the structure one by one and in any position requires emphasis.

The influence of the symmetry upon the ease with which such dual replacements can take place is clearly shown by a contrasting of anorthite with the calcium aluminum garnet. From the former it is only necessary to pass to the other end member (albite) of a conceivably isomorphous series by the substitution of a single group of sodium and silicon atoms for the calcium and aluminum. Because of the large equivalence of chemically like atoms in the cubic garnet several pairs of atoms would have to be interchanged simultaneously in order to obtain a possible end member of such a series. Even then it might happen that in many instances no such end member would be geometrically, not to mention physically, possible. Though the structure of the garnet is not sufficiently well known to permit of a definite statement, it is probable that such a cubic sodium silicon garnet could not exist.

Enough has been said to show that too few data are at hand to give an adequate explanation of isomorphous mixing, even in the relatively simple example of albite and anorthite.

The writer wishes to express his gratitude to H. E. Merwin and to H. S. Washington for discussions of this subject.

RECENTLY DESCRIBED "BISBEEITE" FROM THE GRAND CANYON IS CYANOTRICHITE

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In a recent paper in this journal[1] entitled "The Optical Properties and Morphology of Bisbeeite," Professor Austin F. Rogers described a blue mineral, occurring as minute fibrous spherulites in the Grandview mine, Grand Canyon, Arizona. His identification of the material as representing this species was based on the agreement of his optical data with that for bisbeeite, as determined by W. T. Schaller and recorded in Dana, Appendix 3, p. 14; however, Dr. Schaller informs the writer that the value of 1.65 there given for γ represents an intermediate value between β and γ. Although E. S. Larsen[2] definitely states that he used the original material for a more precise determination of the properties given, Rogers considers it "doubtful whether he worked with the original material." Dr. Larsen informs the writer that not only is his published statement correct, but that he has recently redetermined the values, completely confirming his previous data.

Two very beautiful specimens of this mineral, consisting of methyl-blue capillary crystals, are in the collection of Mr. George Vaux, Jr., Bryn Mawr, Pa., and these were identified optically by the writer as the orthorhombic copper aluminum sulfate, cyanotrichite. They give a copious reaction for sulfur by the usual tests. A comparison of Rogers' data with that of cyanotrichite indicates his material to be that mineral, and not bisbeeite, as may be seen by inspection of the accompanying table.

This conclusion is further substantiated by Rogers' statement: "Although a silicate, it is noteworthy that fragments of the mineral are soluble in a molten sodium metaphosphate bead." As the mineral is a sulfate and not a silicate, this chemical behavior is to be expected.

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[1] *Am. Min.*, **7,** 153–154, 1922.

[2] Microscopic Determination of Non-opaque Minerals, *U. S. Geol. Survey, Bull.* **679,** p. 48.