SCIENCE

VOL. LXI MAY 29, 1925 No. 1587

CONTENTS

SCIENCE: A Weekly Journal devoted to the Advancement of Science, edited by J. McKeen Cattell and published every Friday by

THE SCIENCE PRESS

Lancaster, Pa. Garrison, N. Y.
New York City: Grand Central Terminal.
Annual Subscription, $6.00. Single Copies, 15 Cts.

SCIENCE is the official organ of the American Association for the Advancement of Science. Information regarding membership in the association may be secured from the office of the permanent secretary, in the Smithsonian Institution Building, Washington, D. C.

Entered as second-class matter July 18, 1923, at the Post Office at Lancaster, Pa., under the Act of March 3, 1879.

ATOMS AND ISOMORPHISM

OUR knowledge of the nature of atoms has recently been enlarged in a remarkable way with many important results, some of which were quite unforeseen.

Atoms were formerly known only by their weights and chemical properties. They are now believed to consist of a nucleus and one or more electrons, which together occupy a measurable portion of space. Formerly the properties of atoms were held to be related to the atomic weights. I shall try to show that one of the properties of atoms depends upon their sizes rather than their weights.

The measurement of the sizes of atoms is one of the important results of recent studies of crystals by the new method with X-rays. W. H. and W. L. Bragg[1] reflected X-rays from crystal faces and found that the angle at which reflection became evident bore a simple relation to the wave-length of the X-rays used and to the distance between adjacent layers of atoms in the crystal. The validity of the equation: $\lambda = 2d \sin \alpha$ is easily demonstrated by means of Fig. 1, if it be remembered that the intensity of reflection from a single layer of atoms is extremely small, and the reflected ray only becomes appreciable in case reflections from many parallel planes of atoms are in phase and therefore reenforce each other.

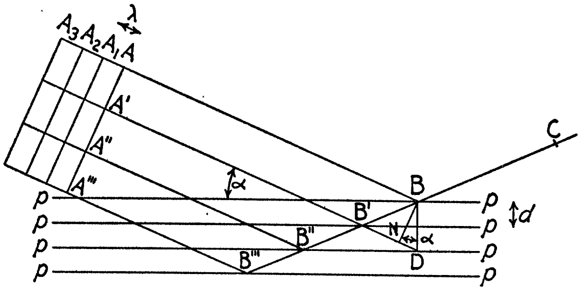

FIG. 1. Reflection of X-rays from a crystal space lattice (after Bragg).

Accordingly, the distance (d) between adjacent planes of atoms is equal to the wave-length (λ) of the X-rays divided by twice the sine of the angle of incidence (α). The wave-lengths of X-rays from various sources are now quite accurately known. Therefore it is only necessary to measure the angle of incidence at which reflection occurs in order to be able to calculate the distance between adjacent planes of atoms in any crystal.

---

[1] "X-Rays and Crystal Structure."

DIMENSIONS OF ATOMS

Atomic "radii" according to W. L. Bragg (*Phil. Mag.* 40, 1920, p. 161) and calculated atomic domains (Ångstrom units)

At. No.	Element	Radius	Volume	At. No.	Element	Radius	Volume
3	Lithium	1.50	14.	28	Nickel	1.35	10.
4	Beryllium	1.15	6.4	29	Copper	1.37	11.
6	Carbon	0.73	1.9	30	Zinc	1.32	9.7
7	Nitrogen	0.65	1.2	33	Arsenic	1.26	8.4
8	Oxygen	0.65	1.2	34	Selenium	1.17	6.8
9	Fluorine	0.67	1.3	35	Bromine	1.19	7.
11	Sodium	1.77	23.	37	Rubidium	2.25	48.
12	Magnesium	1.42	12.	38	Strontium	1.95	31.
13	Aluminum	1.35	10.	47	Silver	1.77	23.
14	Silicon	1.17	6.8	48	Cadmium	1.60	17.
16	Sulphur	1.02	4.5	50	Tin	1.40	12.
17	Chlorine	1.05	4.9	51	Antimony	1.40	12.
19	Potassium	2.07	37.	52	Tellurium	1.33	9.8
20	Calcium	1.70	21.	53	Iodine	1.40	12.
22	Titanium	1.40	12.	55	Cæsium	2.37	56.
24	Chromium	1.40	12.	56	Barium	2.10	39.
25	Manganese	1.47	13.	81	Thallium	2.25	48.
26	Iron	1.40	12.	82	Lead	1.90	29.
27	Cobalt	1.37	11.	83	Bismuth	1.48	13.

In this way the exact arrangement of the atoms in nearly all crystallized elements has been accurately determined. The same method has given similar data for many crystallized binary compounds and for a few crystallized ternary substances. The problem becomes much more difficult of solution with increasing complexity of composition, but important progress is being made even with substances containing several elements.

There is no conclusive evidence yet discovered to prove that atoms are closely packed in crystals. However, it is now generally agreed that atoms in crystals are probably either in contact or close-packed, that is, not far apart.

If atoms are in contact[2] in crystals it is evident that the shortest distance between adjacent planes of atoms in a crystallized substance which consists of atoms of only one element is equal to the diameter of the atom. Professor W. L. Bragg was the first to make use of this fact, and to compile from all the known data a table of the diameters (or radii) of the atoms, as shown below, and graphically in Fig. 2.

Present theories of an atom picture it as composed of a nucleus surrounded by one or more shells of electrons; they therefore permit the assumption, as a first approximation, that atoms are nearly spherical in shape. If so, the approximate volume of any atom can be calculated easily from the table of diameters and the formula: $V = 4/3\, \eta R^3$. In this expression the "volume" is intended to denote not a portion of space solidly occupied by the atom, but that portion of space required for its existence, which is doubtless equal to all the space within the outermost shell of electrons. Some writers have called this volume the atomic "domain" and Tutton has named it the "sphere of impenetrability."

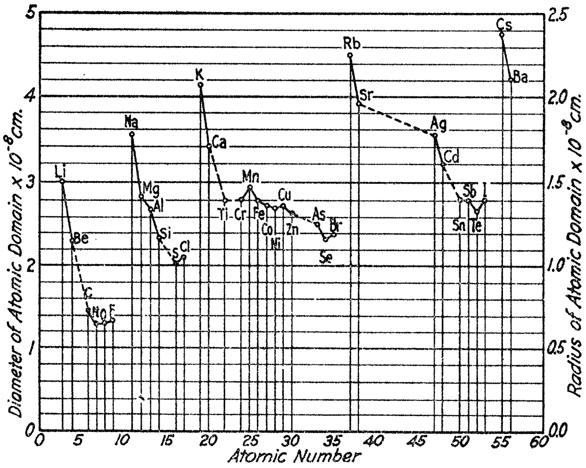

FIG. 2. Atomic domains of elements (after Bragg).

The size, volume or *domain* of an atom is the newly discovered physical property whose importance is

---

[2] If atoms are packed closely together in crystals, but are not in contact, the "volumes" of various atoms, as obtained from the "diameters" or "radii," are slightly greater than the true volumes of the atoms, but represent correctly the portions of space required for the existence of the atoms in crystals.

not yet appreciated by many scientists. It is not supposed to be absolutely constant, like the atomic weight, but, if variations occur under varying physical conditions, they probably do not exceed 25 or 30 per cent., and may be assumed to affect all atoms in about the same way, so that, relatively, the different kinds of atoms vary still less in size.

It is important to note that the atomic domains are not proportional to the atomic weights, but in any series (of the periodic classification) decrease with increasing weight, and, in general, show the same periodic relation to the weight as do all other physical and chemical properties, as shown in Fig. 2. In general, the atoms of electronegative or acid elements are much smaller than those of electropositive or metallic elements. Atoms of the same group (of the periodic classification) are not of the same size, but increase in size with increase of weight. In any series the size decreases with increasing valence.

In the study of crystals it was long ago learned that they are composed of units which are definitely and uniformly arranged throughout a single crystal. Indeed, the precise number of possible types of crystals was determined many years before all these types were found, by a mathematical solution of the problem of finding all possible arrangements of points in space such that the arrangement about any one point is the same as (or else a mirror image of) the arrangement about any other point. Nearly all solid mineral substances are crystalline, so that this condition of very exact arrangement of the units in a solid is the normal state of substances which are not liquid or gaseous. Any given substance solidifying under given conditions always produces crystals of exactly the same kind. It is a natural consequence of the precise arrangement of the units of structure in crystals that they are bounded by smooth faces; and, furthermore, that the angles between similar faces are exactly the same on all crystals of the same kind. Finally, with some exceptions, the interfacial angles of any substance are different from those of any other substance. This is so true that the great Russian mineralogist, Federoff, has recently published elaborate crystallographic tables[3] by means of which he has been able to completely identify many substances by crystal measurements alone.

However, some substances form crystals whose angles differ only slightly from those of the crystals of certain other substances. Two substances whose crystals are nearly the same in shape are said to be "isomorphous," which means that they are characterized by having the same forms. This term "isomorphism" was applied to such a condition when it was supposed that the forms were exactly the same; it is now demonstrated that they differ, though the difference may be very slight.

Substances which form crystals of almost exactly the same shape are nearly always closely related in chemical composition. For example, the following substances illustrate four isomorphous groups:

I	II	III	IV
$CaCO_3$	$CaSO_4$	$MgFe_2O_4$	$MgFe_2O_4$
$MgCO_3$	$SrSO_4$	$FeFe_2O_4$	$MgAl_2O_4$
$FeCO_3$	$BaSO_4$	$ZnFe_2O_4$	$MgCr_2O_4$
$MnCO_3$	$PbSO_4$	$NiFe_2O_4$	
$ZnCO_3$			

It was a natural conclusion from these and similar facts that in an isomorphous series only those changes of composition are possible in which one element replaces another of the same valence.

In the light of our new knowledge of the precise structure of crystals this conclusion needs revision, as I shall attempt to show in the following discussion.

Isomorphism is a comprehensive term, which is generally understood to apply to all cases of chemically similar substances which have similar crystal forms. No one has ever defined the amount of chemical or crystallographic similarity necessary to constitute isomorphism. However, it is generally agreed that intercrystallization to form homogeneous crystals composed of two (or more) substances in any proportions whatever illustrates the most perfect isomorphism. There is considerable evidence to prove that the crystal forms in such cases are very nearly alike, but the limits of possible variation are not accurately known. In other cases one substance can take into its crystal structure up to say 40 per cent. of another substance, but not more. These may be considered cases of imperfect or partial isomorphism. In still other cases one substance can take into its crystal structure (or into "crystal solution") very small amounts of another, perhaps no more than 5 per cent. These may be considered cases of very limited isomorphism.

Reverting to the X-ray study of crystals, it may be recalled that such studies have led to the conclusion that crystals are built of atoms which are in contact, or close packed. Furthermore, in any crystal each kind of atom occupies certain definite positions, so that, for example, a crystal of NaCl consists of atoms of Na in a definite arrangement intergrown with atoms of Cl in a definite arrangement, as shown in Fig. 3. Such definite arrangements of atoms, whether of one kind or several kinds, are known as "space lattices." That is, the NaCl space lattice con-

---

[3] Memoire Acad. Sci. Russie, Phys. Math. ser. 8, XXXVI, 1920.

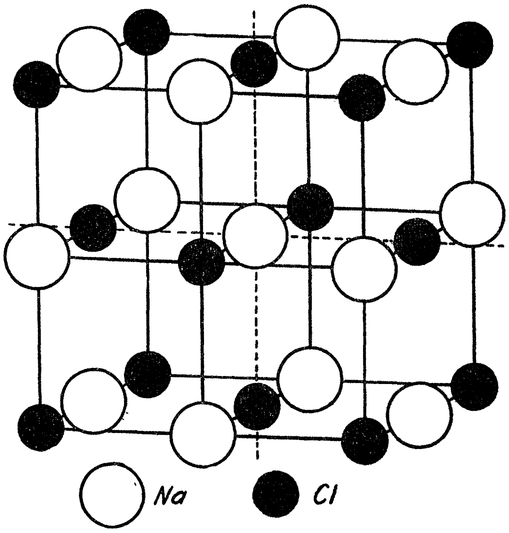

Fig. 3. Space lattice of sodium chloride.

sists of two parts—a regular space lattice of Na atoms intergrown with a regular space lattice of Cl atoms. Neither one of these space lattices can exist alone, but, if it could, it would make a crystal of the same type and symmetry as the interpenetration of the two, and just as perfect a crystal, except for the voids occupied in the NaCl crystal by the atoms of the other space lattice. If any atoms other than those of Na or Cl exist in a NaCl crystal (not merely mechanically enclosed) they must either replace some of the atoms of the NaCl space lattice, or be small enough to find places between these, as very fine sand can find places between the grains of very coarse sand, even though the latter are in contact. Both these cases probably occur in crystals, but it is plainly only the first case which can lead to an isomorphous series. For example, if a NaCl crystal contained some NaBr, not mechanically mixed, but as an integral part of the crystal, the Na space lattice would not be changed at all, but the Cl space lattice would be different in that some of the points occupied by Cl atoms in a pure NaCl crystal would be occupied by Br atoms. With a gradual increase in the relative number of Br atoms a series can be imagined extending from pure NaCl to pure NaBr.

In general, all crystals, whose detailed structure is now known, are similar to those of NaCl in consisting of two (or more) interpenetrating space lattices. Any one of these is just as definite and regular as any other.

Now, if crystals are close-packed space lattices built out of atoms, and if isomorphous systems can be formed only by replacement in the space lattice of one kind of atom by another, it is evident that the size (or domain) of the atoms must be very important in determining what atoms can mutually replace one another in such systems. This principle, that atoms must be of nearly the same size in order to be able to form isomorphous systems in various compounds, seems to be far more important than the old idea that the atoms must be of the same valence. In every substance forming a crystal or an end-member of an isomorphous system all valences must be satisfied, but it does not follow from this that the replacing atoms must be of the same valence. For example, in feldspars, $NaAlSiSi_2O_8$ and $CaAlAlSi_2O_8$ are end-members of a perfect isomorphous series in which Na and Si of the first substance are replaced by Ca and Al of the second. That is, a monovalent and a tetravalent atom are replaced by a divalent and a trivalent atom. This leads to a complete isomorphous series, because the volumes of Na and Si are nearly equal to the volumes of Ca and Al.

The feldspars also illustrate the point that size of atoms is more important than equal valences or other chemical similarities. Thus, $NaAlSi_3O_8$ and $KAlSi_3O_8$ are two well-known feldspar molecules which differ only in one atom—Na or K—and the change here is from one alkali to another alkali element of the same valence and similar chemical characters. Nevertheless, $NaAlSi_3O_8$ and $KAlSi_3O_8$ exhibit only imperfect or partial isomorphism,[4] while $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$ form a perfect isomorphous series.

Similar conditions seem to exist in every group of isomorphous minerals[5] which is fully known. Thus, in the garnet group there are six end-member molecules which belong to two systems,[6] rather than one, as follows:

---

[4] It is an interesting fact that, in this case and in some others, two substances, whose unlike atoms differ so much in size that the isomorphism is only partial at ordinary temperature, exhibit perfect isomorphism at high temperature, as if the expansion of the space lattice due to heat were sufficient to permit free replacement of the smaller atoms by larger ones at high temperature, even though that is impossible at low temperature.

[5] An apparent exception is presented in the case of the zeolites (and certain other hydrous minerals) which are capable of exchanging bases with those of salts in a solution in which they are immersed under the control of valence and independent of the size or number of the atoms concerned. The writer believes that this is possible only *after formation* of the crystals and that atomic volume relationships are in control during the formation of the crystals in this case as in the case of all anhydrous minerals. He has presented the evidence for this view in the *American Mineralogist*, Vol. X, 1925.

[6] H. Boeke: *Zeit. Krist.*, LIII, 1914, p. 149.

I	II
$Ca_3Al_2(SiO_4)_3$	$Mg_3Al_2(SiO_4)_3$
$Ca_3Fe_2(SiO_4)_3$	$Fe_3Al_2(SiO_4)_3$
$Ca_3Cr_2(SiO_4)_3$	$Mn_3Al_2(SiO_4)_3$

The members of each system are mutually miscible (in crystals) in all proportions, since Al, Fe and Cr are similar in size, and also Mg, Fe and Mn, but the members of one system show only partial miscibility with members of the other system, since Ca has nearly twice the volume of Mg, Fe or Mn.

Again, in the calcite group, which consists of $CaCO_3$, $MgCO_3$, $FeCO_3$ and $MnCO_3$, $CaCO_3$ is not miscible in more than very limited amounts with any of the other substances, and the latter are mutually miscible in all proportions, on account of the unequal size of Ca as compared with the other—nearly equal—bases. $CaCO_3$ forms double salts with the other molecules, but these are not evidence of miscibility, since they have entirely different symmetry; even if they were considered evidence of miscibility, $CaCO_3$ could not be considered miscible with the other molecules except in certain quite limited ranges of proportions, and not in all proportions, like the other molecules of the group.

Many isomorphous groups of natural silicates are only imperfectly known, and the true explanation of the variations in their composition, that is, the exact formulas of the end members of the systems, are still under discussion. This is not the place even to summarize such discussions, and I am therefore forced to assume responsibility for my statements in such cases, rather than to pursue the more satisfactory method of presenting the evidence.

In the melilite group of minerals the chief molecules are:[7] $Ca_2MgSi_2O_7$ and $Ca_2Al_2SiO_7$, while other molecules include $Ca_2FeSi_2O_7$, $Ca_2Fe_2SiO_7$, $Ca_2MnSi_2O_7$, $Ca_2ZnSi_2O_7$, and probably $Ca_3Si_2O_7$ and $Na_2Si_3O_7$. All these molecules, except the last two, seem to be mutually miscible in all proportions. According to the results of experiments made here last year by Wanenmacher and Kyle $Na_2Si_3O_7$ is miscible in $Ca_2MgSi_2O_7$ to about 30 per cent., and $Ca_3Si_2O_7$ to about 5 per cent., or, in the presence of $Na_2Si_3O_7$, to about 20 per cent.

The nephelite group consists of $NaAlSiO_4$ and $KAlSiO_4$, with which $CaAlAlO_4$ seems to be miscible[8] in limited amount.

Melilite[9] and nephelite both seem to illustrate the second method by which foreign atoms can enter a space lattice. That is, both commonly contain a limited amount of excess SiO_2, which is demonstrably not essential to the crystal, and in one case has been shown to increase the specific gravity in proportion to its abundance.

The scapolite group[10] brings out one more point of importance. The chief molecules are: $NaCl.3NaAlSi_3O_8$ and $CaCO_3.3CaAl_2Si_2O_8$, which may also be written: $Na_4Al_3Si_3Si_6O_{24}Cl$ and $Ca_4Al_3Al_3Si_6O_{24}CO_3$. That is, Na and Si are replaced by Ca and Al as in feldspar, and also one atom of Cl is replaced by the CO_3 group. If the volume of the CO_3 group could be considered as equal to the sum of the volumes of the atoms concerned the total would be about the same as that of Cl, but *considered as a group* the volume of CO_3 is evidently much greater, and approaches $3/4\ \eta$ times the cube of the sum of the radius of C plus the diameter of O. Therefore, it seems probable that in this case Cl is replaced by C and the extra oxygen atoms occupy interatomic spaces, like the atoms of SiO_2 in nephelite and melilite.

One more case must be mentioned. A. E. H. Tutton,[11] of England, has spent a lifetime making a series of crystallographic and optic measurements of extraordinary accuracy on sixty-two salts of the orthorhombic series $R_2(S, Se)O_4$ and the monoclinic series $R_2M(S, Se)_2O_8.6H_2O$, in which R represents K, Rb, Cs, Tl or NH_4 and M represents Mg, Zn, Fe, Ni, Co, Mn, Cu, or Cd. While all the substances in each group are isomorphous in the broad sense of that term, it is important to note that in this case also the extent of miscibility is determined by the relative sizes of the atoms concerned. Thus salts of K are miscible to a moderate extent with those of Rb, but only to a very slight extent with those of Cs. The volume of the NH_4 group is not accurately known, but it must be nearly equal to that of Rb, since Rb and NH_4 salts are miscible in all proportions.

Many other examples could be described, but perhaps more are unnecessary.

In summary, it may be said that, while substances which are chemically closely similar are often isomorphous in the broad sense of that term, the most perfect cases of isomorphism are found among substances which are chemically less closely related, because the relative sizes of the atoms determine the miscibility of substances in crystals, and the atoms which are chemically most nearly alike are not most similar in size.

A. N. Winchell

University of Wisconsin

---

[7] *Am. Jour. Sci.* CCVIII, 1924, p. 375.

[8] The view that $CaAlAlO_4$ is a constituent of nephelite is new and not demonstrated, but it is in harmony with all known facts.

[9] *Am. Jour. Sci.* CCVIII, 1924, p. 375.

[10] Am. Mineral. IX, 1924, p. 108.

[11] "The Natural History of Crystals," London, 1924.