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The Use of Atomic Radii in the Discussion of Interatomic Distances and Lattice Constants of Crystals*

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The system that has been used by various authors in the past for discussing interatomic distances and lattice constants of crystals in terms of atomic radii is described. It is pointed out that in recent papers Geller has discussed the lattice constants of compounds with the β -wolfram structure in a way that deviates from past usage.

The discussion of lattice constants given in two recent papers (Geller, 1956, 1957) is of such a nature as to indicate the need for a recapitulation of the procedure that has been generally used in the past for discussing interatomic distances and lattice constants of crystals in terms of atomic radii.

During past decades many investigators (Bragg, Goldschmidt, Wyckoff, Huggins, and others) have made use of atomic radii in the discussion of interatomic distances in crystals and molecules. It has been found that the distance between two atoms A and B can often be satisfactorily represented as the sum of two terms, r_A and r_B , which may be called the radii of the atoms. There is no doubt that in general the expression of an interatomic distance as the sum of two radii represents a good approximation, and that whenever a deviation from this additivity in interatomic distances is found one should look for a cause for it. In particular, in crystals with different structure the bonding power of the atom may be distributed in different ways among the bonds that it forms. One method of discussing interatomic distances in metals and intermetallic compounds in terms of atomic radii and the nature of the bonds involved has been extensively developed (Pauling, 1947, 1949, 1950).

It may be expected that in a crystal containing elements of two kinds, A and B , various interatomic distances $A-A$, $A-B$, and $B-B$ may be represented as the sum of the two radii corresponding to the two atoms in contact. This additivity of interatomic distances does not, however, lead in general to an additivity in lattice constants†. Let us consider the

two metals copper and gold and their alloys. Copper crystallizes with the cubic close-packed structure with $a_0 = 3.607$ Å, and gold crystallizes with the same structure with $a_0 = 4.070$ Å. The two metals form a complete series of solid solutions with one another, and, on annealing, some of the solid solutions assume ordered structures. In particular, the alloy corresponding to the composition Cu_3Au has the structure with Au at 0, 0, 0 and 3 Cu at $0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2};$ and $\frac{1}{2}, \frac{1}{2}, 0$. This structure is invariant, the only parameter required for its description being the lattice constant a_0 .

Let us predict the interatomic distances that one would expect. The predicted Cu-Cu distance, from the lattice constant for copper, is 2.551 Å, and the predicted Au-Au distance is 2.878 Å. From additivity (using the effective radii 1.276 Å and 1.439 Å for Cu and Au, respectively) we predict for Cu-Au the value 2.715 Å. In the ordered crystal Cu_3Au each gold atom is surrounded by twelve copper atoms, and each copper atom is surrounded by six gold atoms and six copper atoms. There are accordingly, per unit cell, twelve Au-Cu contacts and twelve Cu-Cu contacts. The nature of the structure is such, however, that these contacts cannot have the expected interatomic distances, because the distances are required to be equal, with the value $a_0/2$. We accordingly assume that the interatomic interactions are strained: the Cu-Cu bonds are stretched, and the Au-Cu bonds are compressed. If the bonds of the two different types are assumed to

is such as approximately to permit contact between cations and the anions ligated about them and also between the anions; in consequence, the repulsive forces that operate are larger than those in a crystal with other values of the radius ratio (permitting either effective contact between cations and anions or just between anions), and the equilibrium value of the lattice constant is such as to cause both the cation-anion distance and the anion-anion distance to be larger than the values given by sums of ionic radii. The discussion of the forces of interaction of the ions in these crystals has permitted a theoretical treatment to be developed that leads to the prediction of lattice constants to within about 0.2%, including alkali halogenide crystals with anion contact and those with double repulsion (Pauling, 1927).

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† The alkali halogenide crystals provide interesting examples of deviation from additivity. For several of these crystals the values of the lattice constants correspond to additivity in the cation-anion distances. It was pointed out by Landé (1920), however, that in lithium iodide the lattice constant is determined by contact between the iodide ions, and that the distance between the lithium ion and the iodide ion is several percent larger than the expected contact distance. Also, in several of the alkali halogenide crystals there is 'double repulsion': the ratio of sizes of cation and anion

be represented by potential functions with about the same curvatures, equilibrium would be reached, with equal numbers of bonds under compression and tension, at a value midway between the two predicted interatomic distances; that is, at 2.633 Å.

This argument is in agreement with experiment. The interatomic distance 2.633 Å, when multiplied by the factor $\sqrt{2}$, gives for a_0 the value 3.720 Å, which is almost exactly equal to the experimental value, 3.725 Å.

We see that the lattice constant itself for the compound Cu_3Au is not given additively by the lattice constants of the two elements; instead, it is the weighted average of these lattice constants in the ratio 3:1, which is the ratio of the number of atoms in the formula Cu_3Au . The average interatomic distance in this crystal is not equal to the sum of the effective radii of the two elements Cu and Au, but is instead equal to $\frac{3}{2}r_{\text{Cu}} + \frac{1}{2}r_{\text{Au}}$; that is, to the sum of the radii weighted according to the numbers of atoms of the two kinds in the crystal.

This method of discussing lattice constants of crystals in terms of the weighted averages of atomic radii has a long history. It is identical with Vegard's rule for lattice constants of solid solutions (Vegard, 1921). According to Vegard's rule, the lattice constants of a solid solution containing x_A mole fraction of A and x_B mole fraction of B is $x_A a_A + x_B a_B$. It is seen that Vegard's rule applied to the crystal Cu_3Au leads to the value given above for the lattice constant, in essential agreement with experiment.

Geller (1956) has, however, attempted to discuss the lattice constants of compounds A_3B with the β -wolfram structure in a new and unreasonable way. He has assumed that the lattice constants are equal to the sums of the equally weighted atomic radii of A and B , multiplied by the suitable geometrical factor.

It is my opinion that it is impossible to find a justification for this treatment. It is true that in this crystal each atom B is in contact with twelve surrounding atoms A . Each A is, however, in contact with several other atoms A , as well as with atoms B . The situation is closely similar in nature (although not identical) with that in the compound Cu_3Au discussed above. It is evident that a better treatment of the lattice constants for these compounds can be made by taking the weighted sums of the atomic radii; that is, by multiplying the quantity $\frac{3}{2}r_A + \frac{1}{2}r_B$ by the proper geometric factor. It is this treatment, which agrees completely with the customary use of atomic radii in discussion of interatomic distances and lattice constants, that was used in my paper (Pauling, 1957). It is not surprising that the latter treatment leads to better agreement with experiment (mean deviation 0.004 Å) than the treatment given by Geller (mean deviation 0.010 Å)*.

To illustrate the absurdity of Geller's treatment, we might consider a compound AB_3 . Geller would predict the same lattice constant for this compound as for a compound A_3B . (In fact, no such reciprocal pair of compounds is known at the present time with the β -wolfram structure.) The lattice constant of the disordered solid solution CuAu_3 is found experimentally to be 2.93 Å, in agreement with prediction by Vegard's rule and our method of discussing interatomic distances and lattice constants; it is 0.21 Å greater than the lattice constant for the ordered (or the disordered) phase Cu_3Au .

In his second paper Geller (1957) has mentioned my earlier discussions of interatomic distances in various crystals, such as MgZn_2 and BaAl_4 , with use of the simple additivity rule, and has suggested that this is not compatible with the use of weighted averages in discussing the lattice constants. It is, however, exactly compatible with this use, as is shown by the discussion of Cu_3Au given above.

Geller in both of his papers has expressed his disappointment that a set of atomic radii for metals developed ten years ago (Pauling, 1947) does not, when applied in a simple way, reproduce completely satisfactorily the lattice constants of the compounds with the β -wolfram structure. I myself am disappointed that the discussion of interatomic distances in metals and interatomic compounds is not simple, but requires consideration of such factors as strain in bonds caused by the limitations of the geometry of three-dimensional space, transfer of electrons from one atom to another, and change in hybridization of bond orbitals. I feel that it is a source of satisfaction, rather than of dissatisfaction, that the lattice constants of the 32 compounds with the β -wolfram structure can be given with mean deviation 0.004 Å by taking the weighted means (weights 3:1) for the atoms A and B in the compound A_3B , with use of effective

of a study made by him of the optimum values of the coefficients by which the radii r_A and r_B of the two kinds of atoms in the β -wolfram structure should be multiplied to reproduce the lattice constants of the 32 compounds. He expressed the lattice constant as $a(\alpha r_A + \beta r_B)$, with $\alpha + \beta = 2$, and evaluated the parameters a , α , and β by the method of least squares. In the first calculation he used for the radii the values of $R(L = 12)$ proposed in 1947 (Pauling, 1947). The result of this calculation was

$$a_0 = 1.7811 \times (1.4221r_A + 0.5779r_B).$$

He then used the coefficients obtained in this way for a least-squares evaluation of the radii of the 20 elements in the 32 compounds. These radii were found to have a mean deviation from the radii $R(L = 12)$ of 0.025 Å, with the greatest deviation 0.057 Å. He then used the new values of the radii for a least-squares re-evaluation of the coefficients, obtaining the result

$$a_0 = 1.7808 \times (1.4185r_A + 0.5815r_B),$$

These least-squares evaluations give for the ratio of the coefficients of r_A and r_B the values 2.46/1 and 2.44/1, respectively, which are far closer to the ratio 3/1 corresponding to the assumption made by Pauling (1957) than to that 1/1 of Geller (1956).

* Dr E. W. Hughes has kindly reported to me the result

radii of the 20 elements involved that differ by such a small amount as 0.025 Å (mean deviation) from the metallic radii for ligancy 12 that were formulated for the metals in 1947.

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Comments on the Preceding Paper by L. Pauling Entitled "The Use of Atomic Radii, etc."

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The writer believes that his position regarding the various aspects of the β -W type structure has been made abundantly clear in his two papers (Geller, 1956, 1957) and therefore, that there is no point in his further discussing this most recent paper (Pauling, 1957).

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The Crystal Structure of AgClO_2

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The structure of AgClO_2 has been determined, using the Fourier difference method to locate the chlorine and oxygen atoms. The crystals of AgClO_2 are orthorhombic, with four molecules in a unit cell. The lattice constants are $a = 6.07$, $b = 6.13$, $c = 6.68$ Å, all ± 0.01 Å, space group $D_{2h}^{21}-Cmma$. The structure is built up of AgClO_2 molecules, rather than of Ag^+ and ClO_2^- ions.

Introduction

The salts of chlorous acid represent a field which has been little studied from a structural point of view. Of preceding research, that of Levi & Scherillo (1931; see also Wyckoff, 1951) on NH_4ClO_2 is considered the most complete. This salt has high symmetry (tetragonal) but decomposes in a few hours and cannot tolerate long exposure to X-rays.

This paper describes the study of AgClO_2 , which with $\text{Pb}(\text{ClO}_2)_2$ represents the only anhydrous chlorite which gives distinct crystals. AgClO_2 is also the most

stable salt of chlorous acid. Of other chlorites, $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$ is being studied.

Experimental

AgClO_2 crystallizes in flat, rectangular laminae, or rarely in rectangular parallelepipeds, with cleavages parallel to (001) and (010). The crystals, which are a shiny yellow upon preparation, become slightly black in time. Optical examination along the z axis reveals a strong birefringence, with $n_x > n_y$. The X-ray