not arise if the 3·05 A. distance were not a hydrogen bond but simply a close van der Waals approach.) The second difficulty is the small angle required between some hydrogen bonds (67° and 70°). It is possible that these two difficulties are related. In the structure of glycine, Albrecht & Corey (1939) have proposed that 'split' hydrogen bonds can be formed, so that one hydrogen atom can cause the close approach of more than one oxygen atom. The angle between these bonds is 69°, close to the small angle found in racemic acid.

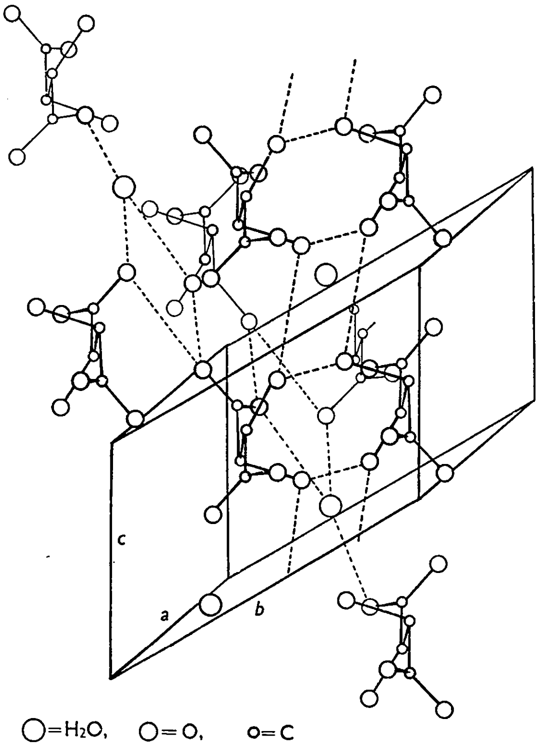

Fig. 12. A drawing of the structure. The broken lines represent the proposed hydrogen bonds.

It is possible, therefore, that split hydrogen bonds may occur here, although in view of the alternative explanation of the first difficulty this can only be a tentative suggestion.

This work forms part of an approved Thesis for Ph.D. in London University. I would like to thank Dr C. H. Carlisle and Dr G. J. Pitt (who suggested the form of the extinction correction) for some helpful discussions at various stages in the work. I am indebted to the Department of Scientific and Industrial Research for a maintenance allowance.

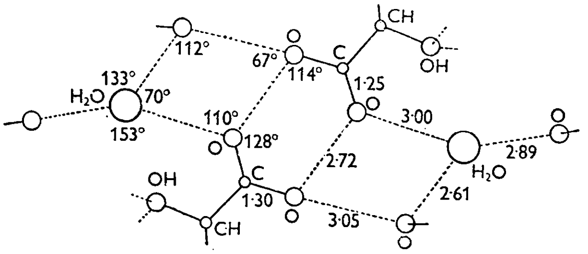

Fig. 13. The proposed arrangement of hydrogen bonds in the plane group containing the water molecule.

References

Albrecht, G. & Corey, R. B. (1939). *J. Amer. Chem. Soc.* **61**, 1087.

Astbury, W. T. (1923). *Proc. Roy. Soc.* A, **104**, 219.

Beevers, C. A. & Hughes, W. (1941). *Proc. Roy. Soc.* A, **177**, 215.

Beevers, C. A. & Stern, F. (1948). *Nature, Lond.*, **162**, 854.

Gerstäcker, A., Möller, H. & Reis, A. (1927). *Z. Krystallogr.* **66**, 421.

Goldschmidt, G. H. & Pitt, G. J. (1948). *J. Sci. Instrum.* **25**, 397.

Groth, P. (1906–19). *Chemische Krystallographie.* Leipzig: Engelmann.

Harker, D. & Kasper, J. S. (1948). *Acta Cryst.* **1**, 70.

Morrison, J. D. & Robertson, J. M. (1949). *J. Chem. Soc.* p. 980.

Pasteur, L. (1848). *Ann. Chim. (Phys.)*, **24**, 28.

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Interatomic Distances in Co_2Al_9*

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It is pointed out that the system of metallic radii leads to interatomic distances in good agreement with those observed for the compound Co_2Al_9.

In a recent paper Mrs A. M. B. Douglas (1950) has reported the results of her careful determination of the structure of the intermetallic compound Co_2Al_9. In this compound each cobalt atom is surrounded by nine aluminum atoms, at the average distance $2{\cdot}47_0$ A. Mrs Douglas, in her paper, stated that 'Corrections

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* Contribution No. 1448 from the Gates and Crellin Laboratories.

applied to interatomic radii derived from the pure metals by Pauling's method predict an average Co–Al distance of 2·615 A, which, though nearer the observed value of $2{\cdot}47_0$ A. [than is the average of the values for the two elements], is still rather high'. This statement seems to have resulted from a misunderstanding of the method, as is shown by the following discussion.*

The single-bond radius of normal cobalt is 1·162 A. and that of aluminum is 1·248 A. (Pauling, 1947, 1949). If cobalt is sexivalent in this compound, as it is in the element and in most other compounds, the bonds to the nine aluminum ligates have bond number $n = 2/3$. The correction $-0{\cdot}600 \log n$ is hence equal to 0·106 A. The sum of these three numbers, 2·516 A., is the value predicted for the Co–Al distance in Co_2Al_9, on the basis of the simplest theory, that the electronic structure of the compound is closely similar to the structures of the two metals cobalt and aluminum. This predicted value, 2·516 A., is in not bad agreement with the observed value, $2{\cdot}47_0$ A., being 0·046 A. high, rather than 0·145 A. high, as is the value quoted by Mrs Douglas.

The distance between aluminum atoms can also be calculated. Each aluminum atom has two cobalt ligates and, on the average, eight aluminum ligates. Aluminum is normally tervalent, and 4/3 valences are used in the two bonds to cobalt, leaving 5/3 to be divided among the eight bonds to the aluminum ligates. The corresponding bond number, 0·208, leads to a correction of 0·409 A. and to the predicted Al–Al distance 2·905 A., which is 0·065 A. higher than the observed average, $2{\cdot}84_0$ A.

A more refined calculation can also be made. It often occurs that adjustment of the electronic structure such as to decrease the interatomic distances takes place in intermetallic compounds. In the compound Co_2Al_9 the principal adjustment that would be expected is a transfer of some electrons from the cobalt atoms to the aluminum atoms (this is in the opposite direction to the transfer of electrons proposed by Raynor & Waldron (1949)). There are three arguments that favor the occurrence of this electron transfer. First, if electrons are transferred from cobalt to aluminum the valence of cobalt remains unchanged, at the value 6 characteristic of the transition elements, whereas the valence of aluminum is increased, and accordingly there results an over-all increase in valence and in the strength of bonds in the intermetallic compound. Secondly, the structure of the normal metallic cobalt atom, as in the elementary substance, represents resonance between the states *A* and *B* in Table 1 in the ratio 35 : 65, as indicated by the saturation magnetic moment 1·71 Bohr magnetons.

Table 1. *Valence states of cobalt*

Co	*A*	↑	↑	↑	●	●	●	●	●	●
Co	*B*	↑↓	↑	●	●	●	●	●	●	○
Co^+	*C*	↑	↑	●	●	●	●	●	●	○

The removal of one electron from the cobalt atom would produce state *C*, in which there are six bonding electrons, a metallic orbital, and two unpaired atomic electrons, corresponding to the saturation magnetic moment 2·00. There would accordingly result an increase in multiplicity for the atomic electrons from the removal of an electron from the cobalt atom, and this would be accompanied by an increase in stability in the system. This argument suggests that between one-half and three-quarters of an electron would be removed from each cobalt atom, on the average, inasmuch as the maximum multiplicity for the transition elements occurs in the region between one-half and three-quarters of the way from cobalt to iron. Thirdly, cobalt is more electronegative than aluminum (electronegativity about 1·8 for cobalt, 1·5 for aluminum) and accordingly the covalent bonds between cobalt and aluminum would have ionic character such as to give a negative charge to the cobalt atoms and a positive charge to the aluminum atoms. The electro-neutrality principle permits the prediction that transfer of electrons from cobalt to aluminum would then occur, in order to restore the resultant charges essentially to zero.

These arguments and the empirical information available about the structure of intermetallic compounds do not permit the completely reliable prediction of the extent of electron transfer from cobalt to aluminum. However, there exists empirical evidence that under these conditions one electron would be removed from each cobalt atom. Let us calculate interatomic distances for Co_2Al_9 on this assumption. The cobalt atom with one electron removed would have the structure *C* of Table 1. The calculation of the single-bond radius for the atom requires knowledge of the amount of *d* character of the bond orbitals. If the metallic orbital were not used for the cobalt atom the bonds would be formed by six d^3sp^2 orbitals with 50% *d* character. While it is conceivable that the metallic orbital of cobalt is not used in this compound (the six bonds of cobalt undergoing pivoting resonance), it seems more likely that the utilization of the metallic orbital is the same as in elementary cobalt: 65% utilization of the set of orbitals d^3sp^3, including a metallic orbital, and 35% utilization of the six bond orbitals d^3sp^2. The amount of *d* character then becomes 45·3%, which leads to the single-bond radius 1·120 A. and to the predicted cobalt-aluminum distance 2·474 A., in exact agreement with the observed value, $2{\cdot}47_0$ A. The valence of aluminum has been increased to $3\frac{2}{9}$ by electron transfer, and accordingly the average bond number of the aluminum–aluminum bonds has been increased to 0·237. This leads to the calculated value 2·872 A. for the Al–Al distances, in essential agreement with the observed value $2{\cdot}84_0$ A.

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* Mrs Douglas's calculated value may have resulted from a misapplication of Table 2 of my 1947 paper. This paper contains corrections to be added to the radius for ligancy 12 to give the radii for other ligancies, the valence remaining constant. I regret that a statement was not included in the paper that care must be taken in using the table in the prediction of interatomic distances for bonds between atoms with different valence.

The Co–Al distances determined by Mrs Douglas vary somewhat about the average value discussed above. The variations might be attributed either to differences in bond numbers or to differences in the amount of d character of the cobalt orbitals. Their distribution in the crystal (especially the 180° angle between the strongest bonds) indicates that the second rather than the first effect is mainly involved. The smallest observed distance, 2·375 A., would result from a 2/3 bond with the cobalt bond orbital having 60% d character. The possibility of unequal distribution of d character among the bond orbitals permits a variety of behavior of the transition elements that is not shown by elements such as aluminum.

Additional experimental evidence about the electronic structure proposed here for Co_2Al_9 could be obtained by study of the magnetic properties of the substances. The above theory requires that the magnetic moment of cobalt in Co_2Al_9 be greater than in the elementary substance, whereas the theory of Raynor & Waldron requires that it be less.

References

Douglas, A. M. B. (1950). *Acta Cryst.* **3**, 19.
Pauling, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.
Pauling, L. (1949). *Proc. Roy. Soc.* A, **196**, 343.
Raynor, G. E. & Waldron, D. M. B: (1949). *Phil. Mag.* **40**, 198.

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The Crystal Structure of α-Monoclinic Selenium*

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The crystal structure of α-monoclinic selenium has been determined by the application of the Harker–Kasper phase inequalities and two-dimensional Fourier syntheses. The α-selenium molecule is an eight-membered, puckered ring similar to the rhombic sulfur molecule. It conforms, within the limit of experimental error, to the non-crystallographic point-group symmetry $\overline{8}2m$; the covalent bond distance is 2·34 ± 0·02 A., and the covalent bond angle is 105·3 ± 2·3°. Certain abnormally short packing distances are observed which are discussed in terms of the metallic character believed to be present in the intermolecular bonding of hexagonal selenium.

Introduction

Selenium exhibits a polymorphism comparable with that of sulfur in complexity. The familiar selenium of commerce is vitreous and can readily be converted into three crystalline polymorphs. A solution of vitreous selenium in carbon disulfide will yield two red, monoclinic varieties designated α and β respectively. Very slow cooling of vitreous selenium which has been heated to a fluid state will produce gray, hexagonal selenium, commonly called metallic selenium.

The relations that exist between the various modifications are known only in a qualitative way. Metallic selenium is the stable form at all temperatures up to the melting point (217° C.), and is obtained from any of the other forms on heating. There is no reverse transformation from the metallic form into any other form below 217° C., hence there is no real transition point in the physical-property curves of selenium.

It appeared desirable to investigate the crystal structures of both α- and β-selenium. The polymorphism of the element is confusing without a knowledge of the underlying atomic arrangement. The polymorphic transitions in sulfur are even more involved, and knowledge of crystal structures in the selenium system may benefit study of the sulfur system because of the several types of sulfur–selenium mixed crystals that are formed (Muthmann, 1890; Halla & Bosch, 1930). Von Hippel (1948) has discussed the progressive change in structure and conductivity for the known structures in the sequence oxygen, sulfur, selenium, tellurium, and polonium in terms of resonance between molecular and ionic structures, making use of Pauling's ideas on the metallic bond (Pauling, 1947). The structures of monoclinic selenium add more experimental data to be tested by this point of view.

The present paper, which presents the complete structure determination of α-selenium, is part of a program of this laboratory which it is hoped will clarify the existing gaps in the knowledge of the crystal chemistry of the element selenium.

Experimental procedure

High-purity selenium* was completely converted to the vitreous form by heating to a fluid state and

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* Furnished by the American Smelting and Refining Company, New York, N.Y.