

Structure and Conductivity in the VIB Group of the Periodic System

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tion. In this case the degeneracy would be even greater, and so we can expect stronger bond.

A mathematical difficulty arises if we treat the plane or the space lattice in a similar way, but we hope these difficulties are not insurmountable. In spite of the difference between a real metal and our linear lattice, we can use the latter in some problems, especially those concerning end effects, etc., in the following way. We can construct the total electron density as a function of the distance from one end of the chain. The results show that though the electrons are distributed almost uniformly in the whole chain, there is some deviation near its free end. So we are able to calculate the dipole moment caused by this irregularity. We can take the surface of a metal as if it were built up of the ends of linear chains. Taking into account the crystal structure of the metal, we can make statements about the behavior of the free ends, i.e., the dipole moments of these chains, which determine the dipole moment of the surface, the adsorption on the surface, the work function, etc.

By this method we can treat also the effect of strange atoms built in the lattice at random or systematically (alloys).

Here we can mention that the viewpoint of Pauling in a recent paper,³ taking into account, among the resonating structures, ionic states also, can be compared with ours presented above, since the M.O. method automatically takes into account ionic states.

Detailed calculations will be published in a forthcoming paper.

¹ This is just the reverse of what Bayliss has done, having constructed a "metallic" model for the conjugated polyenes on the basis of the analogy mentioned above (N. S. Bayliss, *J. Chem. Phys.* **16**, 287 (1948)). The authors take this opportunity to thank the Board of Editors for calling their attention to this paper.

² W. E. Duncanson and C. A. Coulson, *Proc. Roy. Soc. Edinburgh* **62A**, 37 (1944).

³ L. Pauling, *Nature* **161**, 1019 (1948).

Structure and Conductivity in the VI_B Group of the Periodic System

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October 15, 1948

UNDER the title quoted above a paper was recently published in your journal by A. von Hippel.¹ In connection with this paper I should like to mention some results in a study on the same subject, carried out during the period 1940-45.

The trigonal forms of selenium and tellurium exhibit a curious abnormality: the coefficient of thermal expansion parallel to the *c* axis is negative. This may be explained as follows.

The attraction forces between the spiral chains—which lie parallel to the *c* axis—increase the valence angles and cause the spirals to lengthen if they approach each other.²

I tried to calculate whether the forces between the spirals would be sufficient to explain this abnormality, if a lattice

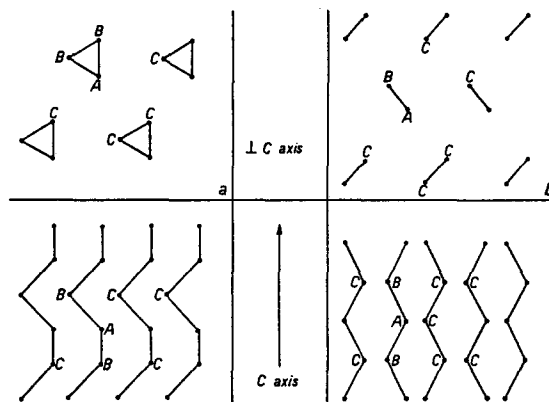


FIG. 1. Comparison of the two lattices. (a) The trigonal spiral chain lattice; the distances are those of the selenium lattice. (b) The hypothetical zigzag chain lattice. Valence angles and atomic radii are the same as in (a). The covalent-bound neighbors of atoms A are indicated by B, the next nearest atoms—van der Waals bound—by C.

were assumed, in which the bonds in the chains were purely covalent, and the bonds between atoms of different chains were of the van der Waals type. The results made it seem probable that the forces between the chains were greater than could be explained by the formulas for the van der Waals-London forces.

This result was caused essentially by the abnormal value of the "van der Waals radius" in the trigonal selenium lattice. The value of this is 1.74Å, whereas the normal value may be considered to be 2.0Å.³

The existence of electrical conductivity made it seem plausible that metallic forces were active here.

Because of war conditions these results had not been published. Meanwhile, the discovery of the cubic form of polonium⁴ added an important indication that forces of the metallic type could determine the form of the selenium and tellurium lattices, as was worked out in von Hippel's paper.¹

Von Hippel chooses for the metallic lattice the simple cubic lattice found in β -polonium. For the covalent type a lattice is assumed which is very similar to the trigonal selenium lattice.

I should like to make a few remarks concerning this latter choice, which may be considered as a further argument in favor of von Hippel's theory. It is possible to construct a lattice, built up from long chains of atoms, which has a larger lattice energy than the spiral chain lattice. If the valence angles, the covalent, and the van der Waals radii are the same in both lattices, the contributions of the van der Waals-London forces will essentially determine the energy difference.

The hypothetical lattice mentioned is the polyethylene type of lattice⁵ and is built up from zigzag chains instead of spiral chains. In Fig. 1 the hypothetical lattice and the lattice actually found are drawn, using the covalent and van der Waals radii known from the trigonal form of selenium, 1.16 and 1.74Å, respectively, for both lattices. From this figure the number of nearest neighbors belonging to different chains may be seen. For the zigzag chains lattice this number is 8, instead of 4 in the spiral chain

lattice, and this number determines the most important term in the contribution to the van der Waals-London energy. For a given value of the valence angles, covalent, and van der Waals radii, the zigzag chain lattice is thus the more stable of the two. To explain why, nevertheless, the spiral chain lattice is found actually, one has to assume that the abnormal radius of 1.74Å could not exist in the zigzag chain lattice. The decrease of the "van der Waals" radius from 2.0Å to 1.74Å would thus be caused by the metallic forces and the existence of these forces in the trigonal form of selenium would make the spiral chain lattice the more stable of the two. From this point of view the peculiar structure of trigonal selenium and tellurium as well as the abnormal value of the van der Waals radius are indications that a simple picture for the lattice forces is not sufficient to describe the situation in these lattices, and a contribution of forces of the metallic type must be taken into account.

¹ A. von Hippel, *J. Chem. Phys.* **16**, 372 (1948).

² F. de Boer, *Rec. Trav. Chim.* **62**, 151 (1943).

³ Linus Carl Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940), p. 176.

⁴ W. Beamer and C. R. Maxwell, *J. Chem. Phys.* **14**, 569 (1946).

⁵ Maurice L. Huggins, *J. Chem. Phys.* **23**, 37 (1945).

The Calculation of Interaction Potentials from Collision Cross-Section Measurements

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A METHOD for calculating interaction potentials from collision cross-section measurements has been presented by J. H. Simons, C. M. Fontana, E. E. Muschlitz, Jr., and S. R. Jackson,¹ and J. H. Simons, E. E. Muschlitz, Jr., and L. G. Unger.² Their method consists essentially of using classical theory and of integrating the collision cross section along the scattering path. They have developed the theory for an interaction potential of the form $V(r) = -K/r^n$, where r is the distance of separation of the centers of mass of the interacting particles. In the present article their method for calculating a correct value of K is shown to be unnecessary; a consistent approximate treatment presented here is entirely satisfactory for the determination of K .

The symbols which will be used are defined as follows:

l = length of the scattering path,

a = radius of the receiver,

b = perpendicular distance from the scattering molecule to the original line of approach of the beam particle,

x = a variable representing distance measured along the scattering path,

TABLE I. The correction factors f'_e and f_e .

m_1/m_2		$\frac{1}{2}$					1				
l/a	5	10	13.89	21.11	63.53		5	10	13.89	28.12	84.71
f'_e	1.000	0.988	0.988	0.994	0.997		1.039	1.003	0.997	0.995	0.997
f_e	0.624	0.697	0.764	0.836	0.939		0.456	0.637	0.712	0.837	0.940

r_0 = distance of closest approach of the interacting particles,

m_1 = mass of the beam particle,

m_2 = mass of the scattering particle,

W = kinetic energy of the beam particle,

$\mu = m_1 m_2 / (m_1 + m_2)$,

ϕ = scattering angle in apparatus coordinates,

K_e = potential constant K obtained from an exact treatment,

K_a = potential constant K obtained from the above authors' approximate treatment,

K_a' = potential constant K obtained by consistent use of small angle assumptions,

$C = \pi^{1/2} \Gamma(\frac{1}{2}n + \frac{1}{2}) / \Gamma(\frac{1}{2}n)$,

$f_e = K_e / K_a$ = the factor by which K_a (determined graphically from the experimental measurements by using the method of the above authors) is multiplied to obtain the correct value of $K = K_e$,

$f'_e = K_e / K_a'$ = the correction factor for obtaining K_e from K_a' which may be determined graphically in the same manner as K_a .

The values of $f_e = K_e / K_a$ reported by the above authors are valid only for a value of l/a of 13.89 which corresponds to the geometry of their particular apparatus.³ The factor f_e is obtained from the appropriate integrals in the manner shown below.

The classical treatment of the scattering problem for two point masses, involving conservation of angular momentum and total energy, yields the following general relation:

$$\int_0^l b^2 dx = \int_0^l r_0^2 dx + (K/W)(m_1/\mu) \int_0^l r_0^{2-n} dx. \quad (1)$$

The exact treatment for the case $n=4$ (the deviation of f_e from unity increases for a given m_1/m_2 and l/a as n increases, and $n=4$ is the largest n value investigated by the above authors) then gives, with $dx = -ad \cot \phi$ and S_n defined as $S_n = (K/W)(m_1/\mu r_0^n)$:

$$\begin{aligned} \int_0^l b^2 dx &= a(K_e m_1 / W \mu)^{1/2} \\ &\times \left[\int_0^{l/a} S_4^{-1/2} d \cot \phi + \int_0^{l/a} S_4^{1/2} d \cot \phi \right] \\ &= a(K_e m_1 / W \mu)^{1/2} (A + B). \end{aligned} \quad (2)$$

The integrals A and B are evaluated graphically.

The above authors' approximate treatment overlooks the r_0^{2-n} integral of Eq. (1) and assumes all collisions to result in small angle scattering. This gives for the case $n=4$

$$\int_0^l b^2 dx = \int_0^l r_0^2 dx = l^3 (\pi K_a / 3aW)^{1/2}. \quad (3)$$

Then by equating the values of the integral, $\int_0^l b^2 dx$, from Eqs. (2) and (3), the above authors' factor f_e is obtained in the form

$$f_e = K_e / K_a = [\pi/3] [(l/a)^3] [\mu/m_1] [(A+B)^{-2}]. \quad (4)$$

However, if the r_0^{2-n} integral is not omitted in an approximate treatment, a completely satisfactory value of K , determined graphically from the experimental data, may be obtained directly. The approximate treatment carried con-