

sidered: those whose trigonal axes project on $[110]$ (type 1) and those whose trigonal axes project on $[\bar{1}\bar{1}0]$ (type 2). We let n_1 and n_2 be the number of Fe^{++} ions per unit volume on sites of types 1 and 2, respectively. After cooling with the applied field \vec{H} along $[100]$, $n_1 = n_2$ and the induced torque is zero. Radiation with \vec{E} parallel to $[110]$ increases n_2 at the expense of n_1 , and $[\bar{1}\bar{1}0]$ becomes the energetically preferred axis. As a result, for \vec{H} along $[100]$, the torque increases. In addition, after this irradiation $n_2 > n_1$; so the optical absorption for \vec{E} parallel to $[\bar{1}\bar{1}0]$ is greater than for \vec{E} parallel to $[110]$.

Irradiation with \vec{E} along $[\bar{1}\bar{1}0]$ reverses the above situation both with respect to torque and with respect to dichroism.

The decay of the dichroism seen in Fig. 2 may be ascribed partly to photoinduced and partly to a thermally activated rearrangement of Fe^{++} ions on octahedral sites. In this connection it may also be remarked that in the absence of light there is a slow spontaneous decay of the induced anisotropy.

From the maximum torque induced (1.60×10^4 dyn cm/cm³) we calculate that $(n_2 - n_1)/n_0 = 0.1$ or

0.5, where n_0 is the total number of Fe^{++} ions per cm³. The number we obtain depends on whether we use $\epsilon = 5$ cm⁻¹ from Ref. 4 or $\epsilon = 1$ cm⁻¹ from Ref. 3.

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¹D. J. Epstein, B. Frackiewicz, and R. P. Hunt, *J. Appl. Phys.* **32**, 2708 (1961).

²R. P. Hunt, *J. Appl. Phys.* **37**, 1330 (1966).

³A. B. van Groenou, J. L. Page, and R. F. Pearson, *J. Phys. Chem. Solids* **28**, 1017 (1967).

⁴R. P. Hunt, *J. Appl. Phys.* **38**, 2826 (1967).

⁵R. W. Teale and D. W. Temple, *Phys. Rev. Letters* **19**, 904 (1967).

⁶U. Enz and H. van der Heide, *Solid State Commun.* **6**, 347 (1968).

⁷W. Lems, P. J. Rijnierse, P. F. Bongers, and U. Enz, *Phys. Rev. Letters* **21**, 1643 (1968).

⁸R. F. Pearson, A. D. Annis, and P. Kompfner, *Phys. Rev. Letters* **21**, 1805 (1968).

⁹D. L. Wood and J. P. Remeika, *J. Appl. Phys.* **37**, 1232 (1966).

DIELECTRIC THEORY OF COHESIVE ENERGIES OF TETRAHEDRALLY COORDINATED CRYSTALS

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Pauling's resonating-bond theory is reformulated in terms of an itinerant dielectric model. In extreme cases discrepancies of more than 200 kcal/mole between the observed cohesive energy and Pauling's value are reduced to 1 kcal/mole. The results completely justify the concept of resonating covalent and ionic contributions to cohesive energies of tetrahedrally coordinated crystals.

The most general theory of the cohesive energies of covalently bonded crystals and molecules is that of Pauling.¹ His basic idea is that the energy of the covalent bond contains two resonating components, a homopolar part and a heteropolar, or ionic, part. The basic parameters in Pauling's theory are derived from his table of elemental electronegativities. In the early work in the 1930's Pauling found it necessary to obtain electronegativities from heterogeneous sources. Bellugne and Daudel² obtained more consistent results using saturated molecules, while retaining Pauling's key assumptions (based on the now defunct Heitler-London model) of additivity for both electronegativity differences and bond energies. In this note, however, a basic restructur-

ing of Pauling's theory is proposed in terms of itinerant dielectric theory. Dramatic improvements in the prediction of cohesive energies of covalent crystals are obtained. In extreme cases the error of more than 200 kcal/mole resulting from the Pauling formulation is reduced to 1 kcal/mole by the new theory.

The resonating character of covalent and ionic components of bond energy, an *ad hoc* element of Pauling's theory, appears naturally in the microscopic dielectric formulation.³ For each covalent crystal one defines an average energy gap E_g which is related to the electronic dielectric constant ϵ_0 by³

$$\epsilon_0 = 1 + (\hbar\omega_p/E_g)^2 A, \quad (1)$$

where $\hbar\omega_p$ is the plasma energy and A is a number of order unity. The crystal pseudopotential is decomposed into a symmetric homopolar part V_S and an antisymmetric heteropolar part V_a . The average matrix elements of V_S and V_a between bonding and antibonding states are denoted by E_h and iC , respectively. Because the structure factor for V_a is 90° out of phase with that for V_S , both E_h and C are real and

$$E_g^2 = E_h^2 + C^2, \quad (2)$$

which reflects the resonating character of homopolar and heteropolar contributions. Representative values for E_h and C for 15 tetrahedrally coordinated crystals have been given,³ and a more complete study of 68 crystals of the diamond, zinc blende, wurtzite, and NaCl types is available.⁴

One can now give a natural definition of fractional covalent- and ionic-bond characters f_c and f_i , respectively:

$$f_c = E_h^2/E_g^2, \quad f_i = C^2/E_g^2. \quad (3)$$

If the resonance concept is valid, then for a given crystal structure, the Gibbs free energy of atomization at STP should have the form

$$\Delta G_s = \Delta E(R)[1 - k(R)f_i]. \quad (4)$$

R labels a row of the periodic table (e.g., $R=3$ for Ge, GaAs, ZnSe) and $k(R)$ is a constant for each R .

Values of f_i are calculated from tabulated⁴ values of E_h and C . Values of ΔG_s are obtained from

$$\Delta G_s(AB) = \Delta G_s(A) + \Delta G_s(B) + \delta G_s(AB), \quad (5)$$

where the elemental cohesive energies $\Delta G_s(A)$, $\Delta G_s(B)$, and the free energy of formation $\delta G_s(AB)$ are obtained from National Bureau of Standards tables.⁵ As shown in Fig. 1, when ΔG_s is plotted versus f_i one finds that (4) is well satisfied.

Consider first $R=1$ (diamond, cubic BN, and BeO). The values of ΔG_s for diamond and cubic BN determine $\Delta E(1)$ and $k(1)$, respectively. One then predicts $\Delta G_s(\text{BeO}) = -244.5$ kcal/mole. The experimental value is -243 kcal/mole. Pauling, on the other hand, gives⁶ in terms of elemental electronegativities X

$$\delta G_s(\text{BeO}) = 92(X_{\text{O}} - X_{\text{Be}})^2, \quad (6)$$

and from (5) one then obtains $\Delta G_s = -468$ kcal/

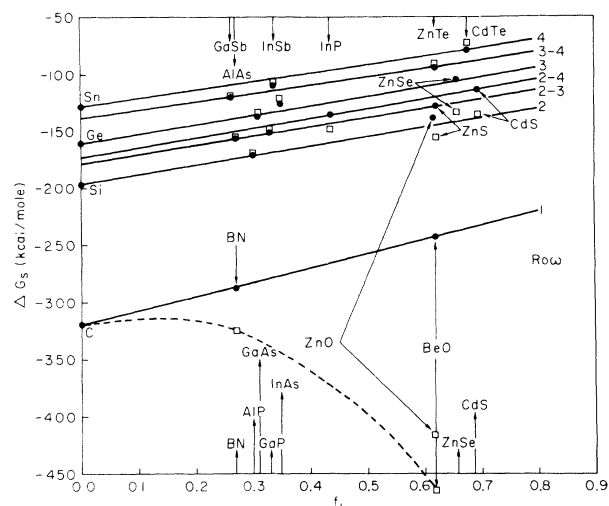


FIG. 1. The difference ΔG_s in Gibbs free energy at STP between the gaseous elements A and B and the crystal AB as a function of dielectrically defined ionic character $f_i(AB)$. Dots, experimental data; open squares, calculation of Pauling.

mole, a discrepancy of more than 200 kcal/mole. This discrepancy is a continuation (see dashed line in Fig. 1) of the error of some 35 kcal/mole in BN. From this example we conclude that the additivity assumptions are too superficial and are inconsistent with the resonating character of the bond, which is genuinely basic. In other cases (such as ZnO) where the electronegativity difference is large, (6) also grossly overestimates the bond strength.

Turning now to the remainder of Fig. 1, we see that the linear resonance relation (4) is well obeyed not only for all rows R but also for mixed cases R_1-R_2 . When there are more than two crystals for a given row, the remaining ones usually fall on the theoretical line to within about 2-3 kcal/mole. A "bad actor" is InAs, which deviates by 13 kcal/mole.

The slopes $k(R)$ are seen to be positive and quite similar in all cases, but because of the high accuracy of the method the differences in slope are meaningful and are shown in Fig. 2. The dip at $R=4$ is associated with resonance between covalent grey Sn and metallic white Sn. This resonance energy decreases as f_i increases for $R=4$, with the result that $\partial^2 \Delta G(R)/\partial f_i^2$ (which is virtually zero for smaller values of R) increases to a maximum value for $R=4$. It is possible that this resonance (which is associated³ with d core states and relativistic contributions⁷ to s - p hybridization energies) also contributes to

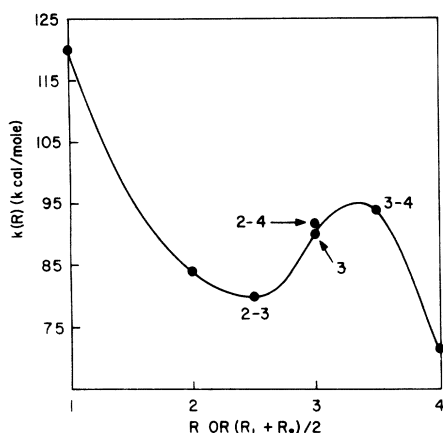


FIG. 2. The slope $k(R) = \partial(\Delta G_s)/\partial f_i$ as a function of row R .

the InAs cohesive energy.

The reader may note the similarity of (2) to the resonant separation of kinetic and potential energies of a simple harmonic oscillator. One may also rewrite (4) as

$$\Delta G_s(R) = \Delta E_c(R)f_c + \Delta E_i(R)f_i, \quad (7)$$

which exhibits the additive nature of covalent and ionic contributions to the cohesive energy.

The accurately linear relations shown in Fig. 1 should have a number of applications. When combined with National Bureau of Standards thermochemical tables⁵ they should facilitate the analysis of binary- and ternary-phase diagrams — e.g., GaAs-GaP. In addition to possible applications, one should note the simple, universal character of the results shown in Fig. 1. In our opinion these results, derived entirely from an itinerant model of the dielectric properties of these crystals, provide a quantum-mechanical justification of the concept of resonating bonds.

The redistribution of charge associated with partial ionicity makes calculation of $k(R)$ difficult. It is instructive, however, to compare the experimental values of $\Delta E(R)$ in (4) with the Fermi energy E_F of a free-electron gas of density equal to that of the valence electrons (Table I). We may regard diamond, where the bonding is almost entirely (sp^3), as normal. In Si the ob-

Table I. Comparison of cohesive energies in kcal/mole in diamond-type crystals with Fermi energy of free-electron gas of density equal to that of the valence electrons.

Crystal	E_F	ΔG_s	$\Delta G_s/E_F$
C	667	320	0.478
Si	287	197	0.685
Ge	265	161	0.607
Sn	210	128	0.608

served cohesive energy is about 50% greater than expected from (sp^3) bonding alone; this is attributed to the effects of $p-d$ valence hybridization. This enhancement is reduced to about 35% by repulsion⁸ between d cores in Ge and Sn.

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¹L. Pauling, The Nature of the Chemical Bond (Cornell University Press, Ithaca, N. Y., 1960), p. 91 ff.

²J. Bellugne and R. Daudel, Rev. Sci. **84**, 541 (1946); cf. H. Pritchard and H. Skinner, Chem. Rev. **55**, 745 (1955).

³J. C. Phillips, Phys. Rev. Letters **20**, 550 (1968).

⁴J. C. Phillips and J. A. Van Vechten, Phys. Rev. Letters (to be published).

⁵F. D. Rossini et al., Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Circular No. 500 (U. S. Government Printing Office, Washington, D. C., 1952); D. D. Wagman et al., Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Technical Note No. 270-3 (U. S. Government Printing Office, Washington, D. C., 1968); C. E. Wicks and F. E. Block, Thermodynamic Properties of 65 Elements — Their Oxides, Halides, Carbides, and Nitrides, Bureau of Mines Bulletin No. 605 (U. S. Government Printing Office, Washington, D. C., 1963); JANAF Thermochemical Tables, edited by Walter H. Jones et al. (Dow Chemical Company, Midland, Mich., 1960).

⁶Our Eq. (6) corresponds to Pauling's (3-13), but with the corrections for N_2 and O_2 multiple bonds omitted. These cancel in computing ΔG rather than δG .

⁷F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall Inc., London, 1963).

⁸J. C. Phillips, Phys. Rev. Letters **22**, 285 (1969).