exchange integral with the nearest-neighbor ions with the ion of interest in an excited state. N/V is the number of spins per unit volume, $\chi_{||}$ the parallel susceptibility, β the Bohr magneton, and g the splitting factor of the ground state.

The results are shown in Fig. 3 where the temperature-dependent change in the splitting is plotted against the experimental susceptibility data of Trapp and Stout.[10] The agreement is again seen to be good, and again the slope corresponds to J_f/J_i equal to 1.3.

A careful examination of the thermal behavior of a magnon sideband to the transition studied above (δ_1 in Ref. 7) was made in an attempt to detect the g factor renormalization of nonzero k magnons suggested by Saslow.[4] The effect could not be detected for this transition in MnF_2.

We wish to acknowledge illuminating communications from Dr. Wayne Saslow and Professor R. M. White, and the loan of a MnF_2 crystal from J. Holzrichter.

[1]W. M. Yen, G. F. Imbusch, and D. L. Huber, in Optical Properties of Ions In Crystals, edited by H. M. Crosswhite and H. W. Moos (Interscience Publishers, Inc., New York, 1967), p. 301.
[2]M. W. Passow, W. M. Yen, and D. L. Huber, Phys. Letters 29A, 156 (1969).
[3]R. M. White, Phys. Letters 19, 453 (1965).
[4]W. M. Saslow, Phys. Rev. Letters 22, 879 (1969).
[5]F. Keffer and C. Kittel, Phys. Rev. 85, 329 (1952).
[6]F. M. Johnson and A. H. Nethercot, Jr., Phys. Rev. 114, 705 (1959).
[7]D. D. Sell, R. S. Greene, and R. M. White, Phys. Rev. 158, 489 (1967).
[8]R. Loudon, Advan. Phys. 17, 243 (1968).
[9]D. D. Sell, thesis, Stanford University, 1967 (unpublished).
[10]C. Trapp and J. W. Stout, Phys. Rev. Letters 10, 157 (1963).

COHESIVE ENERGIES OF TETRAHEDRALLY COORDINATED CRYSTALS*

Linus Pauling†
Departments of Chemistry, Biology, and Physics, University of California, San Diego, La Jolla, California 92037
(Received 12 May 1969‡)

It is pointed out that the statement made by Phillips that large discrepancies exist between the observed cohesive energy of certian crystals and the values calculated by the electronegativity-difference equation is false. The purported discrepancies occurred because of errors in Phillips's calculations.

The first two sentences of the abstract of a recent Letter by Phillips[1] are, "Pauling 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." These discrepancies do not, in fact, exist. The discrepancies reported by Phillips are the result of mistakes made by him in calculating the values.

The substance discussed in detail by Phillips is BeO(c). He states that the experimental value of the free energy of formation of BeO(c) from Be(g) and O(g) is -243 kcal mole^{-1}, and that the value given by my electronegativity-difference equation[2] is -468 kcal mole^{-1}. Phillips made three errors in calculating the latter value: First, an erroneous factor 2 in the term in $(X_{Be}-X_O)^2$ led to an error of -184 kcal mole^{-1}; second, the omission of the multiple-bond correction term for O_2 led to an error of 26 kcal mole^{-1}; third, an error of -37 kcal mole^{-1} seems to have been intro-

duced in some way that is not obvious.

The electronegativity-difference equation for the enthalpy of formation of a normal-valence compound (with no multiple bonds) from the elements in their standard states[2] in kcal mole^{-1} is

$$\Delta H_f^0 = -23\Sigma(X_i-X_j)^2 + 55.4n_N + 26.0n_O, \tag{1}$$

in which the summation is over the single bonds between the unlike atoms i and j with electronegativity values X_i and X_j, and n_N and n_O are the numbers of nitrogen atoms and oxygen atoms in the compound. The terms in n_N and n_O are correction terms for the difference in enthalpy of the multiple bonds in the standard states N_2 and O_2 and single bonds N-N and O-O. For BeO(c), with two Be-O single bonds (resonating among four positions), and with $X_{Be}-X_O = 2$, the corresponding expression is

$$\Delta H_f^0(\text{BeO}) = -2\times23\times4+26 = -184+26$$

$$= -158 \text{ kcal mole}^{-1}. \tag{2}$$

The values of $\Delta H_f{}^0$ of Be(g) and O(g) are 76.6 and 58.6 kcal mole^{-1}, respectively[3]; hence we obtain $\Delta H^0 = -293$ kcal mole^{-1} for the reaction

$$\text{Be}(g) + \text{O}(g) \rightarrow \text{BeO}(c). \tag{3}$$

With the term $-T\Delta S = 20.2$ we obtain $\Delta G^0 = -273$ kcal mole^{-1}, in moderately good agreement with the experimental value[4] -262 kcal mole^{-1}, and far different from the value -468 kcal mole^{-1}, given by Phillips as obtained from Eq. (1).

From Phillips's Eq. (6) it is evident that he used the factor 4 (the ligancy) rather than 2 (the number of single bonds, equal to the normal valence of Be and O) in the first term of Eq. (2), thus introducing an error of -184 kcal mole^{-1}. Also he states in a footnote that he did not make the multiple-bond correction 26 kcal mole^{-1} for the oxygen atom, apparently because of his failure to understand it. With these errors corrected his value becomes -310 kcal mole^{-1}, which differs by -37 kcal mole^{-1} from my calculated value. I have not been able to discover the nature of the third error that he seems to have made.

The "discrepancy of more than 200 kcal mole^{-1}" between Eq. (1) and experiment does not exist. The apparent discrepancy resulted from these errors in calculation made by Phillips.

The other large differences between experimental values of ΔG^0 and the values corresponding to the "calculation of Pauling" shown in Phillips's Fig. 1 seem to be the result of similar errors in his use of the electronegativity-difference equation.

In his Letter[1] Phillips also gives a misleading discussion of another aspect of the theory of the chemical bond. In his Table I he purports to discuss the ratio $-\Delta G^0 / E_F$ of the cohesive energy (Gibbs free energy) of the diamond-type crystals C, Si, Ge, and Sn to the "Fermi energy E_F of a free-electron gas of density equal to that of the valence electrons." He obtains for this ratio the value 0.478 for C, 0.685 for Si, 0.607 for Ge,

and 0.608 for Sn, and concludes that p-d valence hybridization causes an increase in cohesive energy over the sp^3 value (assumed for diamond) of 50% for Si and 35% for Ge and Sn. The values of $-\Delta G^0$ in the table are the free energy of binding for 2C, 2Si, $\cdots$. The values of E_F given in the table are not, however, those of the Fermi energy of the corresponding eight valence electrons, but are those of the energy of one electron at the top of the coupled band of energy levels, differing by a factor 5/24. The corrected values of the ratios are 0.100 for C, 0.143 for Si, 0.126 for Ge, and 0.127 for Sn. The virial theorem suggests that a ratio near unity for $-\Delta H^0 / \Delta E_F$ might be found, where ΔE_F is the difference in mean kinetic energy of the product and the reactants; but it is difficult to justify the neglect of the mean kinetic energy of the reactants [2C(g), etc.], and the ratios 0.100 to 0.143 differ so greatly from unity as to suggest that Phillips's argument, even when corrected, has no validity.

[1]J. C. Phillips, Phys. Rev. Letters 22, 645 (1969).

[2]L. Pauling, The Nature of the Chemical Bond (Cornell University Press, Ithaca, N.Y., 1960), 3rd ed., Eq. (3-13); see also 1st and 2nd Eds., 1939 and 1940.

[3]The experimental values are from Selected Values of Chemical Thermodynamic Processes, National Bureau of Standards Circular No. 500 (U.S. Government Printing Office, Washington, D.C., 1952). The values in JANAF Thermochemical Tables [edited by Walter H. Jones et al. (Dow Chemical Company, Midland, Mich., 1960)] agree to within ±3 kcal mole^{-1}.

[4]Phillips gives -243 kcal mole^{-1} as the experimental value of ΔG^0 for Eq. (2). The National Bureau of Standards Circular No. 500 values give -261.6 and the JANAF values give -260.8.