the initial state yielded spectra at 80°K and 298°K in satisfactory agreement with experiment.

The quantum-mechanical zero-point energy must be considered in deriving the spectra at low temperatures. Examination of the potential energy contours for the ground and excited states reveal that both systems are harmonic oscillators; therefore, the energies of the vibrational levels are[2]

$$E_n = \hbar(k/M)^{\frac{1}{2}}(n+\frac{1}{2}),$$

where k is the force constant obtained directly from the energy contours, and M is the effective mass derived as the following function of the masses of Cl^- and K^+:

$$M = 6M_{Cl^-} + 6\alpha^2 M_{K^+},$$

where α is a coupling constant equal to 0.4264. With the quantum number n equal to 0, the zero-point energy is found to be 0.00830 ev for the ground state and 0.00513 ev for the emitting state.

An exact calculation of the spectra involves summing over the matrix elements for all initial vibrational levels combined with all final vibrational levels, weighted according to a Boltzmann function for the initial levels. This calculation is being investigated. However, because the accessible final vibrational levels involve n of the order of 50, the final state may be considered classically by the correspondence principle, and only the initial state need be considered quantum mechanically. The absorption spectrum is

$$P(\Delta E) = C \sum_{n=0,1,2\cdots} \frac{\exp(-E_n/kT)}{2^n n!} |H_n(\xi_n)|^2 \exp(-\xi_n^2) \frac{\partial a_n}{\partial \Delta E},$$

where C is a normalization constant, ΔE is the transition energy from the nth initial level to the potential energy contour for the final state, $H_n(\xi_n)$ is the nth hermite polynomial of ξ_n, and

$$\xi_n = (Mk)^{\frac{1}{2}}/\hbar^{-\frac{1}{2}}(a_n - a_0),$$

where a_n is the configuration of the nth initial level yielding the transition energy ΔE, and a_0 is the equilibrium configuration of the ground state.

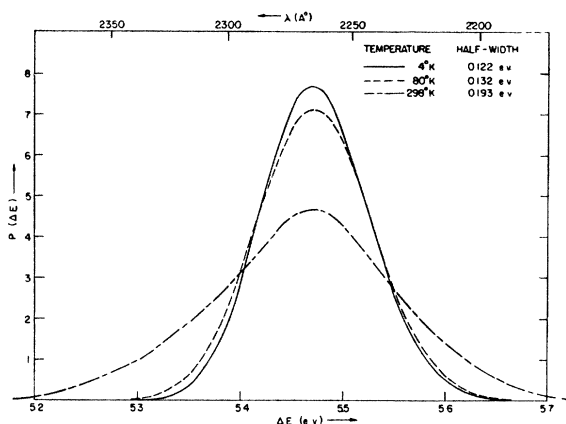The computed absorption spectra at 4°K, 80°K, and 298°K are shown in Fig. 1. The spectra at 80°K and 298°K differ only

FIG. 1. Theoretical absorption spectra of KCl:Tl at 4°K, 80°K, and 298°K.

slightly from the classical results.[1] It is predicted that reducing the temperature of KCl:Tl below 80°K will not appreciably narrow the absorption band. Similar considerations apply to emission. Experimental measurements are in progress in this laboratory to test these predictions. The author is indebted to M. H. Hebb for helpful discussions.

[1] F. E. Williams, Phys. Rev. 80, 306 (1950); J. Chem. Phys. 19, 457 (1951).
[2] Eyring, Walter, and Kimball, Quantum Chemistry (John Wiley and Sons, Inc., New York, 1944), p. 75.

Correlation Energy and the Heat of Sublimation of Lithium

CONYERS HERRING
Bell Telephone Laboratories, Murray Hill, New Jersey

RECENTLY Silverman and Kohn[1] have published a quantum-mechanical calculation of the heat of sublimation of metallic lithium. This calculation, based on the Wigner-Seitz approach, corrects some numerical errors in the previous literature and introduces further refinements. In spite of these, they report a discrepancy of about 4 kcal/mole between theoretical and experimental values of the binding energy. One is therefore faced with the question: is the discrepancy due to some combination of errors in the experimental value and easily correctible short-comings of the theory, or does it indicate a basic inadequancy of the Wigner-Seitz approach, as has been suggested by Kuhn and Van Vleck[2] in the case of the heavier alkali metals? The object of this letter is to show that the former is the case, the discrepancy being primarily due to underestimation of the correlation energy term in the theory and to adoption of too large a value for the experimental heat of sublimation.

In the Wigner-Seitz method one obtains a solution of the self-consistent field problem for an assembly of electrons moving in the superposition of the potential fields of all the ions of the crystal.[3,4] The correlation energy may be defined as the difference between the energy of this self-consistent field solution and the true ground-state energy of an assembly of electrons moving in the given ion core fields. In the past it has usually been assumed that the correlation energy for metal electrons is the same as for a free electron gas of the same density, for which fairly reliable estimates are available.[5,6] However, if the electrons in the metal have an effective mass m^* appreciably different from the true electron mass m, it is obviously more correct to use the correlation energy for a gas of free particles of mass m^*. This procedure must be correct in the limiting case of a hypothetical metal with a very small number of electrons per atom, since the coulomb matrix elements and energy differences among pairs of low energy determinantal wave functions will be asymptotically the same as for free particles of charge e and mass m^*, and since Macke[6] has shown that a quite satisfactory value of the correlation energy can be derived from a variational expression involving only the matrix elements and energy differences between states whose excitation energy is of the same order as the Fermi energy per particle. Since electrons with energies≫those of the first Brillouin zone behave on the average as expected for mass m, the correlation energy for a half-filled zone may be expected to be intermediate between the values for m and for m^*, probably closer to the latter. For mass m^*, Wigner's[5] expression for the correlation energy becomes $0.58/(r_s + 5.1m/m^*)$ rydbergs per electron, where r_s is the radius of the sphere equivalent to an atomic cell. For lithium, $m/m^* = 0.727$[1], and the correlation expression just written exceeds the free electron value by 0.014 rydbergs per atom or 4.3 kcal/mole.

The coulomb and exchange energies, for which Silverman and Kohn also assumed the free electron values, differ from these values by amounts which, though smaller than the above, are worth mentioning for completeness. Seitz[4] has shown that the former exceeds the value for a uniform charge distribution by only about 0.6 kcal/mole. The difference between the exchange energy and that of free electrons of the same density is a little larger: a rough calculation by a formula due to Hill and the author[7] gives a value which is numerically smaller by about 2.2 kcal/mole than for free electrons. As was shown in reference 7, this formula is asymptotically valid for low electron densities, but for the density actually occurring it undoubtedly underestimates the exchange energy. This error tends to compensate the error in the correlation estimate of the preceding paragraph. The exchange correction calculated in this way has the opposite sign from that computed by Seitz.[4] The latter involves a computational error, since the

dominant term in Seitz' expression arises from the second term in his Eq. (25); which can be shown to vanish identically.

On the experimental side, the heat of sublimation can be deduced from the vapor pressure data in the literature,[8] either by using the slope of a vapor pressure plot or by using the third law of thermodynamics together with estimated specific heats for the solid and liquid phases. The two methods do not quite agree, and the second, which gives the lower value, is probably the more accurate. By this method Kelley[9] has obtained a value of 36.1 kcal/mole at 0°K; a more recent but as yet undocumented estimate of 36.5 kcal/mole has been given by the Bureau of Standards.[10]

Table I summarizes the comparison of the theoretical and

TABLE I. Contributions to the binding energy of lithium.

Theoretical, Silverman and Kohn*	34.5 kcal/mole
Coulomb correction	−0.6
Exchange correction	−(2.1 or less)
Correlation correction	+(4.3 or less)
Total	36.0
Experiment, 0°K	36.5

* See the accompanying erratum by Silverman and Kohn; following a suggestion of Professor Brooks a correction for zero point energy amounting to −0.9 kcal/mole has been added.

experimental binding energies. The agreement is closer than the uncertainty in either.

I am indebted to Mr. R. A. Silverman for correspondence relating to these calculations and for communication of the corrected results used in Table I.

[1] R. A. Silverman and W. Kohn, Phys. Rev. 80, 912 (1950).
[2] T. S. Kuhn and J. H. Van Vleck, Phys. Rev. 79, 382 (1950).
[3] E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); 46, 509 (1934).
[4] F. Seitz, Phys. Rev. 47, 400 (1935).
[5] E. Wigner, Phys. Rev. 46, 1002 (1934), Trans. Faraday Soc. 34, 678 (1938).
[6] W. Macke, Z. Naturforsch. 5a, 192 (1950).
[7] C. Herring and A. G. Hill, Phys. Rev. 58, 132 (1940), Eq. (55).
[8] H. Hartmann and R. Schneider, Z. anorg. u. allgem. Chem. 180, 275 (1929); M. Maucherat, J. phys. radium 10, 441 (1939).
[9] K. K. Kelley, U. S. Bureau of Mines Bulletin 383 (1935).
[10] National Bureau of Standards, Selected Values of Chemical Thermodynamic Properties (1950).

Erratum: On the Cohesive Energy of Metallic Lithium

[Phys. Rev. 80, 912 (1950)]

R. A. SILVERMAN
Physics Department, Harvard University, Cambridge, Massachusetts

AND

W. KOHN
Carnegie Institute of Technology, Pittsburgh, Pennsylvania
(Received March 5, 1951)

THE calculations of the letter referred to above were found to contain a numerical error. The corrected Table I of values for the cohesive energy of metallic lithium should now read:

TABLE I.

Method used	Cohesive energy (kcal/mole)
Experimental	36.5
Power series to order k^2	35.2
Variable coefficients using (4)	34.5
Power series to order k^4	35.7
Variable coefficients using (5)	35.4

For the source of the changed experimental value see the letter of Herring in this issue.[1] Furthermore, the theoretical value of Seitz should be changed to 34.5 kcal/mole.

[1] C. Herring, Phys. Rev. 82, 282 (1951).

Erratum: Remarks on the Nuclear Resonance Shift in Metallic Lithium

[Phys. Rev. 80, 913 (1950)]

W. KOHN
Carnegie Institute of Technology, Pittsburgh, Pennsylvania

AND

N. BLOEMBERGEN
Harvard University, Cambridge, Massachusetts
(Received March 5, 1951)

CORRECTION of the same numerical error[1] which affected the letter of Silverman and Kohn, Phys. Rev. 80, 912 (1950), changes the value of P_F to 0.22. The relevant ratio P_F/P_A is thus changed from 1.4 to 1.0.

[1] R. A. Silverman and W. Kohn, Phys. Rev. 82, 283 (1951).

Beta-Alpha-Correlation in the Disintegration of Li^8

J. W. GARDNER
School of Theoretical Physics, Dublin Institute for
Advanced Studies, Dublin, Ireland
(Received February 9, 1951)

BY negative β-decay, Li^8 transforms to Be^8 which is unstable against disintegration into two α-particles. The energy liberated by the entire disintegration Li$^8 \rightarrow 2$He$^4 + e^- + \nu$ is about 15.8 Mev, and the maximum β-energy (W_0) is about 12.5 Mev.[1] Less than 2 percent of the β-disintegrations go straight to the ground state of Be^8, the rest going to an excited state or states of energy around 3 Mev.[2] There is evidence[3–5] for both the values 0 and 2 for the spin of the Be^8*, but the level width is so great (1–2 Mev) that one cannot be entirely certain that there are not two levels present, or, on the other hand, that the properties of a single level of this width need be uniquely defined. Although the two values for the Be^8* spin may not be mutually exclusive, however, it would be useful to see what information the $\beta - \alpha$-angular correlation can give on this point, and, incidentally, on the forbiddenness of the β-transition (whether first or second forbidden).

Any evidence of spin 0 would be of a negative character, since it is a general result of angular correlation theory[6] that an intermediate state of spin 0 means a spherically symmetric angular distribution. It remains therefore to examine what predictions can be made about the $\beta - \alpha$ correlation for a Be^8* spin of 2 and an assignment of the remaining spins and parities, and of the β-forbiddenness, consistent with the experimental evidence. Bearing in mind that Be^8 must have even parity in both the excited state (spin 2) and the ground state (spin 0), and that the transition to the ground state is clearly more forbidden than the transition to the excited state, we are led to conclude that the only likely β-decay schemes for Li$^8 \rightarrow$Be^8* are:

(1) $0+ \rightarrow 2+$, second forbidden (axial vector interaction);
(2) $3- \rightarrow 2+$, first forbidden (axial vector or tensor interaction).

Each of these schemes would be associated with a third forbidden transition to the ground state of Be^8. Of the two possibilities, one would prefer the first, since it assigns even parity[7] to the Li^8, and a second forbidden transition would seem quite consistent with the "ft" value[3] of 2.8×10^5 for this disintegration, when its exceptionally high energy is taken in account.

The $\beta - \alpha$-angular correlation for schemes (1) and (2) has been investigated by the methods of Falkoff and Uhlenbeck;[8] (1) gives a distribution $I_1(\theta) \sim 1 + A_1 \cos^2\theta + B_1 \cos^4\theta$, and (2) a distribution $I_2(\theta) \sim 1 + A_2 \cos^2\theta$. By a general result of reference 8, both distributions must become isotropic for the low energy β-particles, and must show greatest anisotropy as the β-energy W approaches W_0. The coefficient A_2 cannot be evaluated explicitly, since it involves the ratio of unknown nuclear matrix elements; A_1 and B_1, however, involve only one nuclear matrix element, which may be dropped as a common factor. These coefficients