

FIG. 1. Relative integral cross sections (number of stars observed, per target nucleus, with m or more prongs) are plotted for several elements against m, the number of prongs observed. Data for emulsion stars are plotted on a scale of n, the number of prongs actually leaving the disintegrating nucleus (see text).

the data have been replotted against atomic weight for stars of different sizes. The slopes of the lines are indicated, decreasing as smaller stars are included, and probable errors are shown for stars of 4 or more observed prongs. Estimated extrapolation to include stars of all sizes indicates a total cross section close to  $A^{2/3}$ .

Emulsion stars are shown in Fig. 1 for comparison; while their statistical errors are small, for 1630 stars were analyzed, uncertainties exist in (a) the ordinate, which depends on the assumed thickness of the emulsion, and its effective number of atoms per cm<sup>2</sup>. For the latter we have used the equivalent number of atoms of atomic weight 100 (intermediate between Ag and Br) that would give the same cross section as the emulsion constituents, assuming the manufacturer's analysis and a dependence on atomic weight as discussed above. (This equivalent number is not very sensitive to the exponent.) (b) For comparison with the foil curves, the emulsion stars should be plotted on an abscissa of n, the actual number of prongs in the disintegration. The probability, m/n, of detecting a particle from the observed disintegration of a foil nucleus depends on the stopping power and thickness of the foil and the diameter of the field of view, and varies slightly with the position of the disintegrating nucleus in the foil and with the size of the star; but for these foils calculations of this ratio did not vary greatly from an average value of about 2/3.

The resulting emulsion curve approximates, for n > 6, that which one might expect for A = 100. The greater number of smaller stars can readily be accounted for by the known percentages of lighter elements in the emulsion. The average slope of the integral distribution of emulsion stars of 4, 5, and 6 prongs is about 3 times that of the line obtained by projecting to small n the emulsion curve for larger stars (that is, the curve which one would anticipate for A = 100 by comparison with the foil curves). This would indicate that of the small stars found in emulsion, approximately twice as many can be attributed to the lighter elements present as to Ag and Br. There is, however, considerable uncertainty in this value, because the data for small stars in the foils are less reliable; a differential prong distribution will be given upon completion of scanning and rechecking and more careful analysis of corrections. There will also appear an analysis of measurements made on the energy of each particle in the foil stars and the angular distribution to determine their dependence upon atomic weight as compared with theoretical calculations. Only a few "showers" of minimum-ionization particles, usually interpreted as mesons, have been observed, but these yield some information concerning the variation with atomic weight of meson-production



F1G. 2. Integral cross sections vs atomic weight of foil for stars of m or more prongs are shown on a double-log plot for four values of m.

cross sections at these energies. Several students have assisted in this work: James Bailey, Milton Meux, Mel Reed, and Dick Wilson.

\* This work has been aided by a Cottrell Grant from the Research Corporation <sup>1</sup> I. Barbour and L. Green, Phys. Rev. **79**, 406 (1950). <sup>2</sup> P. E. Hodgson, Phil. Mag. **42**, 92 (1951).

## Natural Spread of the Conic Distribution of the Čerenkov Radiation

YIN-YUAN LI Physics Department, University of Illinois, Urbana, Illinois (Received February 26, 1951)

**B**ECAUSE of the existence of a high degree of partial coherence of the wavelets from succeeding free paths the natural of the wavelets from succeeding free paths, the natural spread of the Čerenkov radiation was very much overestimated in a previous letter.<sup>1</sup> The coherent path length of an electron is much closer to the actual length of travel in the material than it is to the mean free path between emissions of quanta. R. L. Mather of Berkeley has observed with proton beams that the half-breadth of the ray directions is less than the minimum predicted in the letter, when the effects of dispersion are removed. He has also observed a rainbow spectrum.

My sincere thanks are due Professor L. I. Schiff and Mr. R. L. Mather for their kind communications.

<sup>1</sup> Yin-Yuan Li, Phys. Rev. 80, 104 (1950).

Theoretical Low Temperature Spectra of the Thallium Activated Potassium Chloride Phosphor

FERD E. WILLIAMS General Electric Research Laboratory, Schenectady, New York (Received March 5, 1951)

FUNDAMENTAL calculation of the absorption and emission spectra of KCl: Tl has been recently reported.<sup>1</sup> From the properties of the constituent ions the potential energy was computed for  ${}^{1}S_{0}$  and  ${}^{3}P_{1}{}^{0}Tl^{+}$  substituted for K<sup>+</sup> in KCl as a function of a precise configuration coordinate, namely, the Tl+ nearest Cl<sup>-</sup> neighbor distance with the condition that the remainder of the lattice rearranges to minimize the total energy. A classical distribution of atomic configurations characteristic of

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<sup>-</sup> and K<sup>+</sup>:

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

where  $\alpha$  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

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

where C is a normalization constant,  $\Delta E$  is the transition energy from the *n*th initial level to the potential energy contour for the final state,  $H_n(\xi_n)$  is the *n*th hermite polynomial of  $\xi_n$ , and

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

where  $a_n$  is the configuration of the *n*th initial level yielding the transition energy  $\Delta E$ , 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.<sup>1</sup> It is predicted that reducing the temperature of KCI: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.

<sup>1</sup> F. E. Williams, Phys. Rev. **80**, 306 (1950); J. Chem. Phys. **19**, 457 (1951). <sup>2</sup> 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

CONVERS HERRING

Bell Telephone Laboratories, Murray Hill, New Jersey (Received March 5, 1951)

**R** ECENTLY Silverman and Kohn<sup>1</sup> have published a quantummechanical 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 shortcomings of the theory, or does it indicate a basic inadequancy of the Wigner-Seitz approach, as has been suggested by Kuhn and Van Vleck<sup>2</sup> 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.<sup>3,4</sup> 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.<sup>5,6</sup> 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<sup>6</sup> 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<sup>5</sup> 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<sup>4</sup> 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 author7 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.<sup>4</sup> The latter involves a computational error, since the