additional photoejection from the outer shells to the bands, so also in the case of the electron absorption we may expect excitations of the outer shell electrons. This could possibly explain some of the cases where there is a correlation between the fine structure and the characteristic spectra but no apparent energy dependence on the lattice.

In order to have a complete theory of the characteristic energy losses in terms of the band picture, more information concerning the densities of states is necessary.

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Cohesive Energy of Potassium*

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The cellular method has been applied to a calculation of the cohesive energy of metallic potassium. The crystal potential is taken from a self-consistent field with exchange for the potassium ion. An approximate exchange interaction between the valence and the core electrons was included. The cohesive energy was found to be 18.5 or 19.3 cal/mole according as Pines' or Wigner's expression for the correlation energy is used, and the effective mass to be 86% of the free-electron mass. The experimental value is 22.6 cal/mole.

INTRODUCTION

THE cohesive energy of potassium was first calculated by Gorin[1] who used the cellular method. Unlike previous calculations for lithium and sodium by Wigner and Seitz[2] and by Seitz,[3] Gorin did not obtain reasonable agreement with experiment, but found a value considerably too small. Gorin attributed the failure to the supposed greater importance of the electron interaction, i.e., correlation between valence and core electrons. The subject has since been taken up again by Kuhn and Van Vleck[4] and by Brooks[5] who use the "quantum defect method" which avoids explicit use of a potential, but rather makes use of knowledge of the energy levels of the free potassium atom, determined by atomic spectroscopy. These authors find much better agreement; in particular Brooks finds a cohesive energy which differs from the experimental value by only 0.4 cal/mole neglecting the Coulomb interactions of the valence electrons—a discrepancy probably well within both the experimental and theoretical uncertainties.

The basic assumption of the Wigner-Seitz method is that the atomic polyhedron can be replaced by a sphere of equal volume. Each atomic cell is regarded as electrically neutral, so that the valence electron moves in the field of the corresponding positive ion. In this approximation, the cohesive energy is essentially the difference of two quantities: first, the boundary correction due to the fact that the wave function of the ground state of the valence electron is flat at the surface of the atomic sphere. Hence there is a decrease in the kinetic energy of the ground-state wave function, and at the same time, the valence electron is forced back into the ion core to a certain extent, i.e., into a region of more negative potential energy. The second quantity is the kinetic energy of the electron distribution, occasioned by the fact that only one electron of each spin can be in a given state. This kinetic or Fermi energy can be calculated by the method of Bardeen[6] (which has been extended by Silverman[7]) where it is determined by the effective mass of the electrons. The contribution from the Coulomb interaction of the valence electrons is considered to be that for a free-electron gas, diminished by the exchange and correlation holes. The net effect of the Coulomb interaction turns out to be small. This surprising result has been explained by Bohm and Pines[8] as a consequence of the screening effect of the rest of the electron distribution on the field of any single electron.

We have repeated Gorin's calculation with some improvements. The potential of the K ion is taken from a self-consistent field with exchange calculated by Hartree and Hartree.[9] (The K^+ ion field used by Gorin

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did not include exchange.) Second, we have used approximate values for the exchange interaction between valence and core electrons, estimated from the Hartree-Fock equations by means of approximate wave functions. Different exchange interactions are used for *s*- and *p*-like states. The value of the cohesive energy obtained, 18.5 or 19.3 cal/mole, according as Pines' or Wigner's expression for the correlation energy is used; is a marked improvement over Gorin's result of 6 cal/mole. Although there is still considerable discrepancy between this value and the experimental result of 22.6 cal/mole,[10] the agreement is reasonable considering the remaining uncertainties. These uncertainties involve: (1) the exact form of the exchange interaction for the valence electron, (2) increased correlation between valence and core electrons over the situation prevailing in the free atom, arising from the compression of the valence electron distribution, (3) polarization of the ion core by the valence electron, (4) deviation of the Coulomb interactions of the valence electrons from the values predicted by the free-electron approximation, (5) terms in the kinetic energy proportional to k^4, and (6) relativistic corrections. It is hoped to consider these topics in a later investigation.

METHOD OF CALCULATION

Approximate wave functions for states of *s*- and *p*-like symmetry were obtained from the orthogonalized plane waves[11] of lowest energy for the type of state considered. These functions were used to compute approximate exchange interactions between core and valence electrons. The *s*-state exchange interaction was included as an inhomogenous term in the wave equation for the Γ_1 state; and the *p*-state interaction was inserted, as a potential, into the equation for the *p*-like functions involved in the effective mass calculation. It can be shown[12] that an exchange interaction can be included in the calculation of the effective mass without change in Bardeen's formula. The difference in the two exchange interactions is significant.[13]

Using this exchange potential and the previously mentioned Coulomb potential from the Hartree field,[9] the wave equation was integrated for the observed lattice spacing ($r_s=4.84$ Bohr units), subject to the boundary condition that the wave function have zero radial derivative on the atomic sphere. An eigenvalue, $E_0=-0.453$ ry, was obtained.

According to Bardeen,[6] the reciprocal of the effective mass, E_2, is given by

$$E_2=\left[\frac{rP^2}{3}\left(\frac{r}{P}\frac{dP}{dr}-1\right)\right]_{r=r_s}. \qquad (1)$$

Here R and P are r times the radial parts of the *s*- and *p*-state wave functions for the energy E_0. E_2 was found to be 1.168, but the value appears to be sensitive to details of the exchange potential in the outer region of the atomic cell. The value obtained by Brooks[5] was 1.065.

The contribution to the binding energy from the boundary correction and from the Fermi energy is

$$E_B=E_0+2.21(E_2/r_s^2). \qquad (2)$$

The value of E_B is -0.342 Rydberg. The contribution from the Coulomb effects in the valence electron distribution is (according to the free-electron approximation)

$$E_I=\frac{1.2}{r_s}-\frac{0.916}{r_s}-\frac{0.88}{r_s+7.79}. \qquad (3)$$

The first two terms represent the Coulomb repulsion and the exchange interaction, respectively. The correlation correction, which is the third term, is that given by Wigner,[14] corrected for an error in Wigner's derivation.[15] The values of these terms are: Coulomb repulsion, 0.2480 Rydberg; exchange, 0.1893; correlation, 0.0697; giving a total of -0.0110 Rydberg, or -3.4 cal/mole. The theory of Pines[8] yields a correlation energy of -0.0671 ry and a net interaction of -0.0084 ry or -2.6 cal/mole.

The cohesive energy is the difference between the sum of E_B and E_I and the ionization energy of the free atom, for which we take the 4*s* electron eignevalue computed by Hartree and Hartree,[16] -0.291 Rydberg. The value obtained is 0.062 Rydberg or 19.3 cal/mole, using Wigner's correlation expression; and 0.059 ry or 18.5 cal, using the result of Pines.

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