

- [1] V. Kasper and G. Pimental, Phys. Rev. Lett. 14, 352 (1965).
- [2] N. G. Basov, V. V. Gromov, and E. L. Koshelev, et al., ZhETF Pis. Red. 9, 250 (1969) [JETP Lett. 9, 147 (1969)].
- [3] K. L. Kompa and G. Pimental, J. Chem. Phys. 47, 857 (1967).
- [4] J. Parker and G. Pimental, H. Chem. Phys. 48, 5273 (1968).
- [5] R. G. W. Norrish, Progr. Roy. Soc. A301, 1 (1967).
- [6] C. Polanyi, Progr. Roy. Soc. A258, 529 (1960).
- [7] J. G. Calvert and J. N. Pitts, Photochemistry, Wiley, 1966.

EQUATION OF STATE OF ALKALI METALS

E. G. Brovman, Yu. Kagan, and A. Kholas

Submitted 28 April 1969

ZhETF Pis. Red. 10, No. 1, 45 - 48 (5 July 1969)

Precision measurements of alkali metals, or more accurately of the isotherms  $\Omega_0(P)$  ( $\Omega_0$  - volume of unit cell), have recently been undertaken in a wide pressure interval [1 - 3]. The results have revealed a sharp deviation from linearity and a nearly universal character of  $\Omega_0(P)$  for various metals, provided the curves are plotted in coordinates  $\Omega_0(P)/\Omega_0(0)$  and  $P/B_{(0)}$ , where  $\Omega_0(0)$  and  $B(0)$  are the volume of the unit cell and the reciprocal compressibility for normal conditions, i.e., at  $P = 0$  and  $T = 0$ . The recently obtained general results on the multielectron theory of metals [4 - 7], which has developed primarily with emphasis on the analysis of the phonon spectra of metals, the binding energies, the compressibilities, and the elastic moduli, makes it also possible to obtain equations of state for nontransition metals. In this case the equation of state is obtained in simple and physically lucid form, which requires no cumbersome band calculations at all. It is of interest to compare the theoretical results with the experimentally obtained data.

The dependence of the pressure on  $\Omega_0$  can be obtained by directly differentiating the expression for the total energy with respect to the volume. In a metal, the static energy (we neglect the zero-point oscillations) can be represented in the form

$$E = E_i + E_e, \quad (1)$$

where  $E_i$  is the energy of a lattice immersed in a homogeneous negative background, and the total energy of the electron system in the field of the fixed ions,  $E_e$ , is obtained in the form of a series in powers of the pseudopotential of the electron-ion interaction,  $V_q$  [4, 5]

$$E_e = \sum_{m=0} E^m. \quad (2)$$

Accordingly, the general expression for the pressure is

$$P = P_i + \sum_{m=0} P^m \quad (3)$$

(for details see [7]). For crystals having cubic symmetry and one atom per unit cell, the value of  $E_i$  is well known. We then obtain readily for  $P_i$

$$P_i = - (Z^2 e^2 / \Omega_0^{4/3}) \xi. \quad (4)$$

( $\xi = 0.480$  for a body centered lattice).

$P^{(0)}$  is the pressure of the interacting electron gas, and  $P^{(1)}$  is the pressure

connected with the non-Coulomb part of the electron-ion interaction (the Coulomb part vanishes because the system is electrically neutral)

$$P^{(1)} = Zb/\Omega_0^2 \quad (5)$$

The constant  $b$  is determined from the limit  $q \rightarrow 0$  for the pseudopotential  $V_q$  that describes the electron-ion interaction

$$V_{\vec{k}} \rightarrow - (4\pi Ze^2/q^2\Omega_0) + (b/\Omega_0) \quad .$$

The remaining terms in (3) are derivatives with respect to the volume of the terms of the series (2) with  $m \geq 2$ , which describe the energy of the indirect interaction between the ions via the conduction electrons [4, 5]. Each term of the series contains the small parameter  $V_k/\epsilon_F$  ( $V_k$  is the value of the pseudopotential at the reciprocal-lattice point) raised to the power  $m$ . In metals such as Na or K, this parameter is very small, making it possible to neglect the multi-ion indirect interaction described by terms with  $m \geq 3$ .

As to the contribution of the pair interaction  $P^{(2)}$ , this term must be taken into account. The corresponding value of the energy  $E^{(2)}$  is given by

$$E^{(2)} = -\frac{\Omega}{2} \sum_{\mathbf{k} \neq 0} |V_{\mathbf{k}}|^2 \frac{\pi(\mathbf{k})}{\epsilon(\mathbf{k})}; \quad \epsilon(\mathbf{q}) = 1 + \frac{4\pi e^2}{q^2} \pi(\mathbf{q}) \quad (6)$$

To determine (6) and (5) it is necessary to know the pseudopotential of the electron interaction. We used a two-parameter model pseudopotential (well at  $r < r_0$ , Coulomb interaction at  $r > r_0$ ), previously introduced in the analysis of the phonon spectrum of metals [5]. The first parameter was determined automatically from the equation  $P = 0$  and the corresponding equilibrium value  $\Omega_0(0)$ , and the second from the experimental value of the shear modulus  $C_{44}$ , which depends on the pseudopotential only via  $V_{\mathbf{k} \neq 0}$ . The determination of  $\epsilon(\vec{q})$  is discussed in [5].

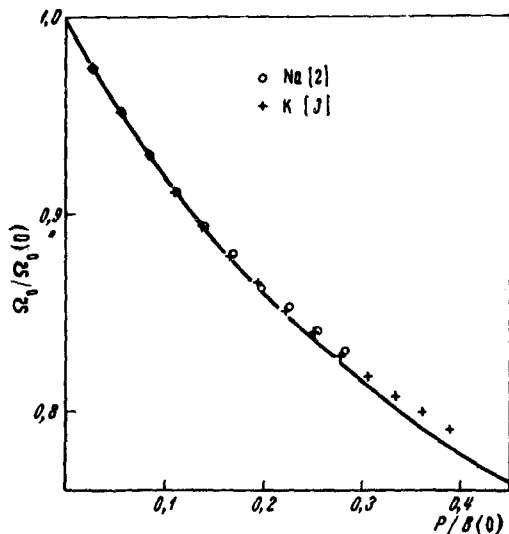
A direct analysis shows that the pressure  $P^{(0)}$  in metals such as Na is small compared with  $P_1$  or  $P^{(1)}$ . To determine this quantity we can therefore use the result of any approximate theory for the electron-gas energy, say the result of Nozieres-Pines [8].

After determining all the contributions to the expression for  $P^{(3)}$ , we can obtain directly the connection between  $\Omega_0$  and the pressure. We shall first demonstrate, however, that the aforementioned universal dependence of  $\Omega_0(P)/\Omega_0(0)$  on  $P/B(0)$  should actually take place in the case of alkali metals. To this end we take into consideration the fact that both  $P^{(0)}$  and  $P^{(2)}$  are small in alkali metals, and make use of the so-called "zero model," i.e., a representation in which the values of  $V_{\mathbf{k}}$  at  $\mathbf{k} \neq 0$  are neglected. We then get approximately from the condition  $P = 0$

$$b \cong \xi z e^2 \Omega_0^{-2/3} \quad (7)$$

Within the framework of the zero model, the reciprocal compressibility is given by (for details see [7])

$$B(P) \cong \Omega \frac{d^2 E}{d\Omega^2} \cong \frac{4}{3} \frac{z^2 e^2}{\Omega_0^{4/3} (P)} \xi + \frac{2zb}{\Omega_0^2(P)} \quad (8)$$



Substituting here (7), we get

$$B(0) = \frac{10}{3} \frac{z^2 e^2}{\Omega_0^{4/3}(0)} \xi. \quad (9)$$

We note that the small term omitted from (8), corresponding to the electronic compressibility, has (like  $P^{(0)}$ ) a dependence on  $\Omega_0$  lying between  $1/\Omega_0^{5/3}$  and  $1/\Omega_0^{4/3}$ , as follows directly from the usual expression for the energy of the electron gas [8]. We can therefore write with good approximation

$$B(0) \sim \frac{1}{\Omega_0^{4/3}(0)}$$

Hence, returning to the general expression for  $P^{(3)}$  and taking (7) into account, we get

$$\frac{P}{B(0)} \cong f \frac{\Omega_0}{\Omega_0(0)}, \quad (10)$$

which is an approximate universal relation for alkali metals. A similar relation was obtained empirically by analyzing the measurements for the entire group of alkali metals [1]. We emphasize that such a simple analysis would not be valid in the general case for an arbitrary metal, owing to the appreciable role of  $P^2$ , and also of the many-particle terms in (3).

The figure shows a theoretical curve for the complete equation of state (with allowance for  $P^{(2)}$  and  $P^{(0)}$  at  $T = 0$ ), in terms of the variables  $P/B(0)$  and  $\Omega_0/\Omega_0(0)$ . The figure shows also the experimental points obtained for Na [2] and K [3]. We see that the agreement between theory and experiment is good in a wide range of applied pressures.

- [1] C. A. Swenson in "Solids under Pressure", McGraw - Hill, 1963.
- [2] R. I. Beecraft and C. A. Swenson, Phys. Chem. Sol. 18, 321 (1961).
- [3] C. E. Monford and C. A. Swenson, J. Phys. Chem. Sol. 26, 291 (1965).
- [4] E. G. Brovman and Yu. Kagan, Zh. Eksp. Teor. Fiz. 52, 557 (1967) [Sov. Phys.-JETP 25, 365 (1967)].
- [5] Yu. Kagan and E. G. Brovman, Neutron Inelastic Scattering (Proc. Symp. Copenhagen) VI, 3, IAEA, Vienna, (1968).
- [6] E. G. Brovman and Yu. Kagan, Zh. Eksp. Teor. Fiz. 57, (1969) [Sov. Phys.-JETP 30 (1967)].
- [7] E. G. Brovman, Yu. Kagan, and A. Kholas, *ibid.* 57 (1969) [30 (1970)].
- [8] D. Pines and P. Nozieres, The Theory of Quantum Liquids, Benjamin, 1966.

#### MAGNETIC SURFACE LEVELS IN SUPERCONDUCTORS

M. Ya. Azbel' and A. Ya. Blank

L. D. Landau Institute of Theoretical Physics, USSR Academy of Sciences

Submitted 12 May 1969

ZhETF Pis. Red. 10, No. 1, 49 - 53 (5 July 1969)

Pinkus [1] has recently pointed out the possibility, in principle, of the existence in superconductors of single-particle bound states due to the penetration of the magnetic field. The physical cause of the appearance of discrete levels is the quantization of the finite motion of the quasiparticles in the potential well produced by the magnetic field near the