[6] A. S. Davydov and G. F. Filippov, J. Exptl. Theoret. Phys. (U.S.S.R.) 32, 945 (1957), Soviet Phys. JETP 5, 773 (1957).

[7] Scharenberg, Stewart, and Wiedenbeck, Phys. Rev. 101, 689 (1956).

[8] G. Bertolini et al., Nuovo cimento 1, 746 (1955).

[9] Baggerly, Marmier, Boehm, and Du Mond, Phys. Rev. 100, 1364 (1955).

[10] Kraushaar, Brun, and Meyerhof, Phys. Rev. 101, 139 (1956).

[11] Kurbatov, Murray, and Sakai, Phys. Rev. 98, 674 (1955).

[12] Benczer, Farrelly, Koerts, and Wu, Phys. Rev. 101, 1027 (1956).

[13] H. Motz, Phys. Rev. 104, 1353 (1956).

[14] A. Alburger and B. Toppel, Phys. Rev. 100, 1357 (1955).

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ON THE THEORY OF THE INTERACTION OF "EXCESS" CHARGES IN IONIC CRYSTALS

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Interaction between polarons is considered. It is shown that the formation of "bipolarons," two polarons separated by a finite distance R and bound by a common polarization, is energetically feasible in crystals with parameters satisfying the condition $n^2/\epsilon \leq 0.05$.

THE interaction of an "excess" electron, introduced into an ionic dielectric, with the crystal polarization oscillations leads, as is known, to the appearance of polaron states.[1] Polarons are majority carriers in ionic crystals; they determine the electrical, photoelectrical, and optical properties of these crystals. Interaction between polarons reduces to electrostatic repulsion and attraction caused by the influence of the inertial polarizational potential well of each electron on the remaining ones (such an attraction will be called hereinafter polarizational in the interests of brevity). Interaction between polarons was not taken into account in polaron theory[1] since it was assumed that the polaron concentration was small enough. The interaction of two electrons in a common polarizational potential well was considered in Refs. 2 and 3. It has been found that such compounds (called bipolarons) do not exist independently of the crystal parameter values. Physically, this means that the Coulomb repulsion force is dominant in this case. However, the electrostatic repulsion and polarizational attraction forces depend differently on the distance between the centers of gravity of the polarizational potential wells and, in general, it cannot be stated beforehand that a stable state of a complex of polarons is impossible when this distance is not zero.

The simplest of such complexes, two interacting polarons, is considered below. The purpose of this work is to explain the possibility of the existence of such a formation. We shall henceforth call it a bipolaron, thus ascribing to this concept a more general meaning than in Refs. 2 and 3. Moreover, our analysis permits an estimate of the influence of polaron interaction on the energy of each polaron and serves therefore as a criterion of whether it is permissible to neglect this interaction for the purpose of formulating a multielectron theory.

The interaction of an "excess" electron with vacancies has also been analyzed; the interaction potential obtained can be used to analyze scattering of carriers by impurities in ionic crystals.

Using the methods developed by Pekar,[1] the Hamiltonian of a system consisting of a crystal with two

electrons introduced therein can be written as follows:

$$\hat{H} = - (\hbar^2 / 2\mu) \Delta_1 - (\hbar^2 / 2\mu) \Delta_2 + U_p(r_1, r_2) + V_p(r_1, r_2) + (e^2 / n^2) r_{12}. \tag{1}$$

Here, the first two terms are the kinetic energy of the electrons, the third term is the interaction energy of the electrons with the inertially polarized crystal, the fourth is the energy of the inertially polarized crystal, and the last is the Coulomb repulsion energy; μ is the electron effective mass, n the optical refractive index of the crystal, r_{12} the distance between the electrons, and the subscripts 1 and 2 refer to the first and second electrons.

The Schrödinger equation with the Hamiltonian (1) can be replaced by an equivalent variational principle. The system energy is then determined by minimizing an appropriate functional dependent on the electron ψ functions and on the specific inertial dielectric polarization **P** created by the excess electrons, subject to the additional condition of normalization of the ψ functions. **P** is first minimized for a fixed ψ in the adiabatic approximation, after which the minimum with respect to ψ is found.

The approximating function was selected in symmetric form:

$$\psi(r_1 r_2) = A [\psi_{a_1}\psi_{b_2} + \psi_{a_2}\psi_{b_1}]; \quad \psi_a = \pi^{-1/2}\alpha^{3/2}e^{-\alpha r_a}; \quad \psi_b = \pi^{-1/2}\alpha^{3/2}e^{-\alpha r_b}; \tag{2}$$

where a, b are centers of polarization potential wells and α is the approximation parameter. The deformation of the ψ cloud of each electron is not taken into account in such a choice of the ψ function. A similar assumption is made, say, in computing the hydrogen molecule by the variational method which, as is known, does not lead to any substantial error.

A computation similar to the above was made by Deigen[4] for the F_2 center, a system consisting of two positive vacancies, separated by a distance R in the ionic crystal, and two polarons. It should be noted that the analysis carried out is not consistently quantum mechanical since the lattice ion motion was considered to be classical. The Deigen[4] results can be used if the terms giving the interaction between the vacancies and the electrons and between the vacancies themselves are cancelled in the Hamiltonian of the crystal — F_2 center system and if R is taken to be the distance between the centers of gravity of the polarized wells.

The functional defining the system energy reduces to the following by substituting (2) and minimizing over **P**:

$$I = (\hbar^2 / \mu R^2) f_1(x) + (e^2 c / R) f_4(x) + (e^2 / n^2 R) f_3(x), \tag{3}$$

where $x = \alpha R$, $c = 1/n^2 - 1/\epsilon$, and ϵ is the dielectric constant; the functions $f_1(x)$, $f_3(x)$, $f_4(x)$ are calculated and tabulated in Ref. 4.

A functional agreeing with (3) was also obtained by Moskalenko[5] who analyzed the problem of a bipolaron from the point of view of the second-quantization method. Moskalenko confined himself only to the tabulation of $I(x, R)$ for certain values of the crystal parameters, which led him to conclude the impossibility of the existence of bipolarons. A more general analysis will be made below which will lead to somewhat different results than in Ref. 5.

To find the stationary states of the system, such values of R should be found for which the function $I(R)$ would have a minimum. The condition $\partial I / \partial R = 0$ leads to the equation

$$- (2\hbar^2 / \mu e^2 R^3) f_1(x) - [c f_4(x) + n^{-2} f_3(x)] R^{-2} = 0. \tag{4}$$

whose roots are

$$R_1 = R_2 = \infty; \quad R_3 = - (2\hbar^2 / \mu e^2) f_1(x) / [c f_4(x) + n^{-2} f_3(x)]. \tag{5}$$

As is easy to verify, minimization of $I(R)$ with respect to x yields the sum of the energies of two polarons in the $R = R_1 = R_2$ case. This case is trivial. Substituting R_3 from (5) into (4), we obtain

$$I(x) = - (\mu e^4 c^2 / 4\hbar^2)(f_4 + f_3 / n^2 c)^2 / f_1. \tag{6}$$

Minimizing (6) with respect to x leads to the relation

$$(f_4 + f_3 / n^2 c) [2 f_1 f_4' + 2 f_1 f_3' / n^2 c - f_4 f_1' - f_3 f_1' / n^2 c] = 0, \tag{7}$$

from which it is not difficult to determine the value of x which yields the minimum value of $I(x)$:

$$n^2 c = u(x); \quad u(x) = - (2 f_3' f_1 - f_1' f_3) / (2 f_4' f_1 - f_1' f_4). \tag{8}$$

We tabulated the first part of (8) for various x. We have $u(x) < 0$ for $x \leq 0.75$. This result is in

$u(x)$

FIG. 1

I, eV

$2J_{pol}$

FIG. 2
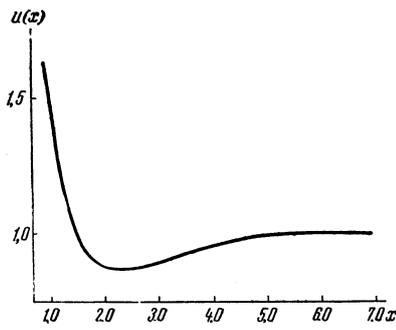
agreement with the conclusion obtained in Refs. 2 and 3 that stationary states of the system do not exist independently of the crystal parameters for $R = 0$ (two electrons in a common polarization potential well). The function $u(x)$ is plotted in Fig. 1 for $x > 0.75\, u(x)$. Using the crystal parameters ϵ and n^2 and Fig. 1, the corresponding value of x_{min} can be found and I_{min} can then be determined from (6).

It follows from Fig. 1 that the solution (6) exists only if $n^2 c > 0.88$ or

$$n^2 / \epsilon < 0.12. \tag{9}$$

and not for arbitrary values of the crystal parameters. The values of ϵ and n^2 for a large number of crystals are cited in Ref. 6, for example. The inequality (9) is not satisfied for all the crystals cited in Ref. 6.

As Davydov[3] and Deigen[7] have shown, the methods of polaron theory are applicable to metal-ammonia solutions. Consequently, our analysis is valid also in this case. The parameters of metal-ammonia solutions ($\epsilon = 22$, $n^2 = 1.76$) satisfy inequality (9). Figure 2 shows a plot of $I(R)$ for such solutions. As is seen from the figure, $I(R)$ has a minimum at $R \approx 4\,A$ and accordingly at $\alpha = 0.42 \times 10^8$ cm^{-1}. However, this minimum appears to be located somewhat higher than the sum of the energies of the two polarons. According to the variational method, a physical meaning should be ascribed to that root of (4) which gives a lower value of the functional being investigated. Consequently, the root $R = R_3$ must be discarded in this case.
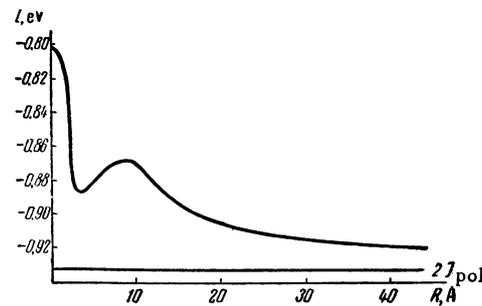
Let us try to explain for which values of the crystal parameters the bipolaron energy (6) becomes less than the sum of the energies of the two polarons, i.e., the relation $I/2J_{pol} > 1$ is satisfied.

Using the value of I according to (6) and J_{pol} from Ref. 1, the criterion for the existence of bipolaron states can be represented as:

$$2.56\,(f_4 + f_3 / n^2 c)^2 / f_1 > 1. \tag{10}$$

The function on the left side of (10) was tabulated for various values of n^2 and c and for the appropriate x obtained by solving (8). The ratio $I/2J_{pol}$ becomes greater than unity for

$$n^2 / \epsilon \leqslant 0.05 \tag{11}$$

and for the appropriate $x = 1.5 - 1.6$. The maximum value of this ratio for $n^2/\epsilon = 0$ is

$$(I / 2 I_{pol})_{max} = 1.08. \tag{12}$$

Hence, the transition of polarons into the bipolaron state is energetically feasible for crystals with values of the parameters ϵ and n^2 satisfying (11). This must be reflected substantially in the properties of such crystals (magnetic properties, formation of color centers, effective mass, and current carrier mobility, etc.).

The approximate wave function of the $e^{-\alpha r}$ kind used above simplifies the computations considerably but is not flexible enough. Since the energy gain calculated above for the bipolaron is small, the results of the computation made require verification by using a more flexible approximation function.

According to Pekar,[1] the best results are obtained with the variational method with one approximation parameter by using a function of the form

$$\psi = A\,(1 + \alpha r)\,e^{-\alpha r}, \tag{13}$$

I, eV

$2J_{pol}$

FIG. 3

which we have indeed used instead of the hydrogen-like functions
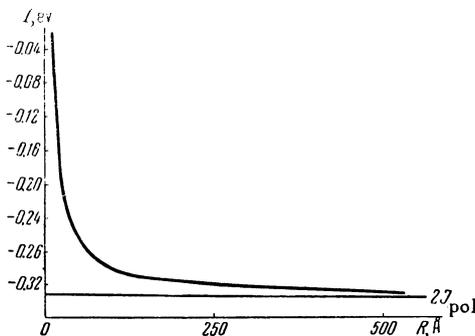
(2a). The functions corresponding to $f_1(x)$, $f_2(x)$, and $f_4(x)$ in (3) cannot be written in explicit form in this case because of the great complexity of the resulting integrals. However, use of the Kopineck[8] results permitted these functions to be tabulated and the solution to be found graphically. The error arising in such a solution is negligible. The numerical results obtained by using (13) are in complete agreement with those cited above [see relations (11) and (12)].

Evidently, taking the mutual deformation of the polarizing potential wells of the interacting carriers into account, as can be done by introducing an additional parameter into the approximating function, can only lead to a less stringent condition on the existence of the bipolaron than (11), since such a parameter affects the calculated bipolaron energy more than the energy of the individual polaron.

The computation carried out can be used to estimate the magnitude of the polaron interaction as a function of their concentration. As an example, we have obtained a configuration curve for KCl (Fig. 3). It is seen from the figure that the polaron interaction is still small at $R \geq 200$ A (this corresponds to an average polaron concentration of the order of 10^{16} cm^{-3}); the error in determining the polaron energy in the single electron problem is not more than 5 percent in such concentrations. This error is $5-20$ percent for concentrations from $10^{16} - 10^{19}$. The error in determining the energy becomes very substantial at concentration $n \geq 10^{19}$ ($R \approx 40$ A in Fig. 3) and the polaron interaction must be introduced into the basic Hamiltonian of the multielectron problem. Incidentally, an appropriate excess positive charge is needed in the crystal to neutralize the excess electrons at such high concentrations and other types of interaction besides the polaron one should be taken into account in the basic Hamiltonian.

ρ (A)	$F(\rho)$ (ev)	$|F(\rho)-J_{pol}|$(eV)	$\frac{e^2}{\varepsilon\rho}$ (ev)
1.64	—1.307	1.142	1.832
3.35	—0.906	0.740	0.897
5.50	—0.672	0.507	0.547
9.81	—0.462	0.297	0.307
13.6	—0.386	0.221	0.222
17.1	—0.341	0.176	0.176
34.2	—0.253	0.088	0.0879
51.4	—0.224	0.059	0.0586
68.5	—0.209	0.044	0.0440
∞	—0.165	0	0

An analysis of an electrically neutral system consisting of a crystal with a vacant lattice site and an electron introduced into the crystal is of interest. The Hamiltonian of such a system is written as

$$\hat{H} = -(\hbar^2/2\mu)\Delta + V_p(r) + U_p(r) - e^2/\varepsilon r. \tag{14}$$

The first term here is the electron kinetic energy, the second is the electron interaction with the polarized crystal, the third is the polarized crystal energy and the last is the electron interaction with the vacancy. Replacing the Schrödinger equation with the Hamiltonian (14) by an equivalent variational principle, we arrive at the corresponding functional. Minimization was made with the aid of a hydrogen-like ψ function of the excess electron. Exactly the same as in the case of two excess electrons, considered above, we can arrive at a functional that is dependent on x and ρ:

$$F = (e^2/\varepsilon\rho)[\hbar^2\varepsilon x^2/2\mu e^2\rho - P(x)], \tag{15}$$

where ρ is the distance between the center of gravitiy of the polarized potential well of the electron under consideration and the "vacancy;" $p(x) = 1 - e^{-2x}(1+x) + (5\varepsilon c/16)x$.

Minimization of F with respect to x was carried out for various fixed values of ρ. The results of a computation for a KCl crystal are cited as an example (see table). Values of the system energy are given in the second column; the third lists the interaction energy between the polaron and the vacancy, equal to $F(\rho) - J_{pol}$, while the fourth gives the values of the Coulomb energy for comparison.

As is seen from the table, the interaction energy between the polaron and the vacancy is notably different from the Coulomb energy only for $\rho < 10$ A.

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[1] S. I. Pekar, Исследования по электронной теории кристаллов (Investigations in the Electron Theory of Crystals), GITTL, 1951.

[2] S. I. Pekar and O. F. Tomasevich, J. Exptl. Theoret. Phys. (U.S.S.R.) 21, 1233 (1951).

[3] A. S. Davydov, Trudy, Physics Faculty Kiev State University 5, 1952.

[4] M. F. Deigen, J. Exptl. Theoret. Phys. (U.S.S.R.) 21, 992 (1951).

[5] S. A. Moskalenko, Уч. зап. Кишиневского ун-та (Sci. Notes, Kishinev Univ.), 17, 103 (1955).

[6] N. F. Mott and R. V. Gurney, Electron Processes in Ionic Crystals, Oxford, 1948 (Russ. Transl.).

[7] M. F. Deigen, Trudy, Phys. Inst., Acad. Sci. Ukr. S.S.R. 5 (1954).

[8] H. J. Kopineck, Z. Naturforsch. 5a, 420 (1950); 6a, 177 (1951); 7a, 785 (1952).

DE HAAS—VAN ALPHEN EFFECT IN A VARIABLE MAGNETIC FIELD

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A theoretical study is made of the characteristic features of the oscillations of the magnetic moment of a metallic specimen at low temperatures in a pulsed magnetic field.

IN connection with the use of the pulse method for the study of the De Haas-Van Alphen effect in strong magnetic fields,[1] it is of interest to clarify the peculiarities of the oscillations of the magnetic moment of a metal at low temperatures in a variable magnetic field of a pulsed type.

In Sec. 1 of the present paper, we give qualitative consideration to this problem, and show that the oscillation properties of the magnetic moment of a metallic specimen in a pulsed field depend essentially on the ratio of the characteristic dimension in the problem of the penetration of the variable field into the metal to the dimension of the sample itself. In Sec. 2 and 3, formulas are obtained for the oscillating part of the magnetic moment for different values of this ratio, and their analysis is given.

1. OSCILLATIONS OF THE MAGNETIC MOMENT OF A METALLIC SAMPLE IN A PULSED FIELD

(Qualitative Considerations)

The oscillations of the magnetic moment of a metal are determined by the quantized motion of the conduction electrons (current carriers) in the magnetic field; their periods and amplitudes are connected with the form of the electron dispersion law near the Fermi surface.[2] There are usually some groups of electrons in the metal with different dispersion laws, and each of these makes its own contribution to the oscillations of the magnetic moment. In what follows, we shall consider the contribution to the oscillating part of the magnetic moment of only one such group of electrons with the particular dispersion law $\epsilon = \epsilon(p)$ (ϵ = energy, p = quasi-momentum of the electron).

If the homogeneous field H is constant, then the oscillating part of the magnetic moment* of the electron gas is given by the following formula:[2]

$$M_{\rm osc} = V \sum_{n=1}^{\infty} \Psi_n(H) \cos\left(\frac{\alpha n}{H} + \varphi_n\right); \tag{1}$$

V = volume occupied by the electron gas (the volume of the metal); $\Psi_n(H) \equiv \Psi_n(H, T)$ = some slowly changing function of H and the temperature T; $\alpha = c S_m(\zeta)/e\hbar$, where $S_m(\zeta)$ = the ex-

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*We are considering the component of the magnetic moment in the direction of the magnetic field.