

EFFECT OF RESONANCE EXCITATION TRANSFER IN THE THEORY OF A LARGE RADIUS EXCITON

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Submitted to JETP editor September 8, 1958

J. Exptl. Theoret. Phys. (U.S.S.R.) **36**, 1703-1708 (June, 1959)

A theory for large-radius excitons is proposed, which takes into account Coulomb as well as resonance interaction. A transition to continuum, made under certain assumptions, leads to an integro-differential equation that contains a nonrelativistic contact term.

There are two limiting mechanisms for the travel of an exciton through a crystal. The first, indicated by Frenkel¹ is due to the presence of resonance interaction, and consists of the vanishing of the excitation at one point of the crystal and its occurrence at a different point, while the width of the exciton zone, and consequently also the group velocity of the exciton motion, remain finite as the overlap integrals tend to zero. The second mechanism enters into the Wannier-Mott theory of large-radius excitons^{2,3} and consists of the displacement of an electron and a hole through the crystal; the electron and hole are considered as quasi-particles with a specified dispersion law, which describes the structure of a definite electron and a definite hole zone (or a definite group of electron and hole zones). Therefore the width of the exciton zone tends to zero, when the exchange integrals that determine the width of the electron and hole zones become annihilated. The first mechanism of exciton displacement will be called "resonant," and the second "exchange."

In the Wannier-Mott theory no account is taken of the ability of the electron-hole pairs of becoming annihilated or created. Consequently, the dependence of the structure of the exciton zone on the strength of the transition oscillator becomes lost, as do other features, and a contradiction with general theory⁴ arises as regards the structure of the exciton band in the vicinity of the point $k = 0$. In the present communication we introduce annihilation terms in the large-radius exciton theory and consider the results therefrom.

We consider a dielectric, and build up its electron wave function in accordance with the orthogonalized system of the Wannier quasi-atomic functions. Let φ_{pg} and φ_{pe} be the Wannier functions corresponding to g -th and e -th orbits of the p -th elementary cell. Henceforth the functions φ_{pg}

will pertain to states which are completely filled in the unexcited crystal, and φ_{ne} will pertain to states which are completely free. The elementary cell may have a complicated structure; for example, it may consist of a series of atoms and ions. We do not take spin interactions into account and consider singlet states. Then the matrix element of the Hamiltonian H of the electron system will be

$$\langle pg, ne | H | p'g', n'e' \rangle = \langle pg | H_1 | p'g' \rangle \delta_{ne, n'e'} + \delta_{pg, p'g'} \langle ne | H^1 | n'e' \rangle + M_{pg, p'g'}^{ne, n'e'} + K_{pg, p'g'}^{ne, n'e'} \tag{1}$$

$$M_{pg, p'g'}^{ne, n'e'} = 2 \langle \bar{\varphi}_{p'g'}(\mathbf{r}_1) \bar{\varphi}_{ne}(\mathbf{r}_2) | e^2 / r_{12} | \varphi_{pg}(\mathbf{r}_2) \varphi_{n'e'}(\mathbf{r}_1) \rangle, \tag{1a}$$

$$K_{pg, p'g'}^{ne, n'e'} = - \langle \bar{\varphi}_{p'g'}(\mathbf{r}_2) \bar{\varphi}_{ne}(\mathbf{r}_1) | e^2 / r_{12} | \varphi_{pg}(\mathbf{r}_2) \varphi_{n'e'}(\mathbf{r}_1) \rangle. \tag{1b}$$

Here the symbol $|pg, ne\rangle$ denotes the anti-symmetrized wave function of the crystal, in which the electron has been removed from the orbit pg and transferred to the orbit ne , while the symbols $|ne\rangle$ and $|pg\rangle$ are the wave function of a crystal in which the orbit ne has an excess electron or the orbit pg lacks an electron; $\langle ne | H^1 | n'e' \rangle$ and $\langle pg | H_1 | p'g' \rangle$ are the matrix elements of the Hamiltonian of a crystal containing a zone electron or a zone hole, respectively. Integrals of the type like K_{\dots} and M_{\dots} will be called integrals of the Coulomb type or of the resonant type.

In the quantum state, determined by the set of normalized excitation amplitudes $\{a_{pg}^{ne}\}$, the crystal energy is

$$E \{ \{ a_{pg}^{ne} \} \} = \sum_{n \neq pg} \sum_{n' \neq p'g'} \bar{a}_{pg}^{ne} \langle pg, ne | H | p'g', n'e' \rangle a_{p'g'}^{n'e'}. \tag{2}$$

The contribution to the first two terms of relation (1) to the sum in the right half of (2) can be readily obtained by going over from the quasi-atomic functions to the zone functions:

$$|ke\rangle = N^{-1/2} \sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}} |n\mathbf{e}\rangle, \quad |k\mathbf{g}\rangle = N^{-1/2} \sum_{\mathbf{p}} e^{i\mathbf{k}\mathbf{p}} |p\mathbf{g}\rangle \quad (3) \quad \text{where}$$

(N is the number of elementary cells in the principal region). Then, if we introduce the notation

$$H^{ee'}(\mathbf{k}) = \langle ke | H^1 | ke' \rangle, \quad H_{gg'}(\mathbf{k}) = \langle k\mathbf{g} | H_1 | k\mathbf{g}' \rangle, \quad (4)$$

the sum of the two considered terms will be

$$\sum_{p\mathbf{g}} \sum_{n\mathbf{e}e'} \bar{a}_{p\mathbf{g}}^{n\mathbf{e}} H^{ee'} \left(\frac{1}{i} \nabla_{\mathbf{n}} \right) a_{p\mathbf{g}}^{n\mathbf{e}'} + \sum_{n\mathbf{e}} \sum_{p\mathbf{g}g'} \bar{a}_{p\mathbf{g}}^{n\mathbf{e}} H_{gg'} \left(\frac{1}{i} \nabla_{\mathbf{p}} \right) a_{p\mathbf{g}g'}^{n\mathbf{e}}; \quad (5)$$

the differentiation of a function of discrete argument $a_{p\mathbf{g}}^{n\mathbf{e}}$ is understood in the sense of differentiation of its representation in the form of a Fourier polynomial.

As can be seen from (1), the quantities $M_{p\mathbf{g}, p'\mathbf{g}'}^{n\mathbf{e}, n'\mathbf{e}'}$ are large only when \mathbf{n} and \mathbf{n}' are close to \mathbf{p} and \mathbf{p}' , and diminish exponentially with increasing $|\mathbf{n} - \mathbf{p}|$ and $|\mathbf{n}' - \mathbf{p}'|$; when $\mathbf{n} = \mathbf{p}$ and $\mathbf{n}' = \mathbf{p}'$ they go into the ordinary integrals of resonant interaction, which determine the structure of the exciton zones in molecular crystals.^{1,5} On the other hand, these quantities decrease slowly with increasing $|\mathbf{p} - \mathbf{p}'|$ and the character of their asymptotic behavior at large $|\mathbf{p} - \mathbf{p}'|$ determines many effects that are connected with far interactions. We shall therefore restrict ourselves* here to the expansion $M_{p\mathbf{g}, p'\mathbf{g}'}^{n\mathbf{e}, n'\mathbf{e}'}$ in non-orthogonality integrals, which lead to the relation

$$M_{p\mathbf{g}, p'\mathbf{g}'}^{n\mathbf{e}, n'\mathbf{e}'} = U_{pp'} (\bar{x}_{p\mathbf{g}, i}^{n\mathbf{e}}, \bar{x}_{p\mathbf{g}, ij}^{n\mathbf{e}}, \dots | x_{p'\mathbf{g}', i}^{n'\mathbf{e}'}, x_{p'\mathbf{g}', ij}^{n'\mathbf{e}'}, \dots), \quad (6)$$

where

$$x_{p\mathbf{g}, i}^{n\mathbf{e}} = \sqrt{2} \int \bar{\varphi}_{p\mathbf{g}}(\mathbf{r}) (x_i - p_i) \varphi_{n\mathbf{e}}(\mathbf{r}) d\tau,$$

$$x_{p\mathbf{g}, ij}^{n\mathbf{e}} = \sqrt{2} \int \bar{\varphi}_{p\mathbf{g}}(\mathbf{r}) (x_i - p_i)$$

$$\times (x_j - p_j) \varphi_{n\mathbf{e}}(\mathbf{r}) d\tau \text{ etc.} \quad (7)$$

where $\mathbf{p} = (p_1, p_2, p_3)$ is the position of the \mathbf{p} -th elementary cell and $U_{pp'}(\dots | \dots)$ is the energy of the electrostatic interaction between a system of multipoles (dipole, quadrupole, etc.) located at the point \mathbf{p} , with components $\bar{x}_{p\mathbf{g}, i}^{n\mathbf{e}}, \bar{x}_{p\mathbf{g}, ij}^{n\mathbf{e}}$ etc., and a system of multipoles having components $x_{p'\mathbf{g}', i}^{n'\mathbf{e}'}, x_{p'\mathbf{g}', ij}^{n'\mathbf{e}'}$ etc. at the point \mathbf{p}' . Using (6), and also the fact that the translational symmetry allows us a choice of the amplitudes $a_{p\mathbf{g}}^{n\mathbf{e}}$ in the form $a_{p\mathbf{g}}^{n\mathbf{e}} = N^{-1/2} a_{\mathbf{g}}^{\mathbf{n} - \mathbf{p}, \mathbf{k}} \exp(i\mathbf{k}\mathbf{p})$, we find the third term of the right half of (2):

$$\sum_{p'} U_{pp'} (\bar{X}_i[a], \bar{X}_{ij}[a], \dots | X_i[a], X_{ij}[a], \dots) \exp\{i\mathbf{k}(\mathbf{p}' - \mathbf{p})\}, \quad (8)$$

*The effect of resonance type integrals with $\mathbf{n} = \mathbf{n}'$, $\mathbf{p} = \mathbf{p}'$ on the arrangement of the energy levels of the exciton was investigated by Moskalenko and Tolpygo.⁶

$$X_i[a] = \sum_{\mathbf{n} - \mathbf{p}} \sum_{e\mathbf{g}} a_{\mathbf{g}}^{\mathbf{n} - \mathbf{p}, \mathbf{k}} x_{p\mathbf{g}, i}^{n\mathbf{e}} \text{ etc.}$$

These last quantities determine the matrix elements of the coordinates and of their products for a transition from the ground state into the exciton state with $\mathbf{k} = 0$. For large-radius excitons they are considerably smaller than the analogous matrix elements in isolated atoms, and a simple estimate shows that in this case expression (8) has a smaller order of magnitude than expression (5), which is on the order of an electron volt. Therefore, in the greater part of the Brillouin zone, allowance for (8) leads only to small numerical corrections.

The situation is quite different in the vicinity of the point $\mathbf{k} = 0$, where, owing to the slow convergence of the series, expression (8) becomes a non-analytic and even a discontinuous function of \mathbf{k} . In this region the presence of integrals of the resonance type changes the dispersion law qualitatively. The singular portion of (8), which is of principal interest to us, can be segregated by going over to the macroscopic field;⁷ the regular portion will be disregarded henceforth. In this approximation, (8) has the form, accurate to terms of order k^2 ,

$$\frac{4\pi e^2}{v k^2} \left\{ \frac{1}{1!1!} \bar{X}_i[a] X_j[a] k_i k_j - \frac{i}{1!2!} (\bar{X}_i[a] X_{js}[a] - X_i[a] \bar{X}_{js}[a]) k_i k_j k_s + \left[\frac{1}{2!2!} \bar{X}_{ij}[a] X_{st}[a] - \frac{1}{1!3!} (\bar{X}_i[a] X_{jst}[a] + X_i[a] \bar{X}_{jst}[a]) \right] k_i k_j k_s k_t + \dots \right\}. \quad (9)$$

Here v is the volume of the elementary cell of the crystal; repeated coordinate indices imply summation. The first term in (9) is in full agreement with the general result of Pekar.⁴ It can also be readily compared with the formula obtained in models that are essentially close to that of Frenkel.^{8,9*}

The matrix elements $K_{p\mathbf{g}, p'\mathbf{g}'}^{n\mathbf{e}, n'\mathbf{e}'}$ decrease exponentially with increasing $|\mathbf{p} - \mathbf{p}'|$ and $|\mathbf{n} - \mathbf{n}'|$, while the diagonal elements are the ordinary integrals of Coulomb interaction. Since we plan to consider large-radius states, in which the average distance between the electron and the hole exceeds considerably the lattice constant, we expand $K_{p\mathbf{g}, p'\mathbf{g}'}^{n\mathbf{e}, n'\mathbf{e}'}$ in non-orthogonality integrals and retain only the first term

$$K_{p\mathbf{g}, p'\mathbf{g}'}^{n\mathbf{e}, n'\mathbf{e}'} \approx -\delta_{n\mathbf{e}, n'\mathbf{e}'} \delta_{p\mathbf{g}, p'\mathbf{g}'} \frac{e^2}{|\mathbf{n} - \mathbf{p}|},$$

corresponding to the Coulomb attraction between

*An error in writing down the system of equations analogous to (1) has crept into the paper by Wannier,² and led to a loss of the resonance-type integrals and of all the singularities due to the far-interaction effect.

the point charges, omitting higher terms that lead to the appearance of nondiagonal matrix elements and tensor forces.

Inserting the resultant expressions into (2) and varying over the excitation amplitudes, we obtain an infinite system of equations, from which it is possible to determine in principle the wave functions and the energy spectrum. In practice, however, it is more convenient to carry out a certain transformation, which facilitates further transition to continuum and to the effective-mass approximation.

We use the representations $|\mathbf{ne}\rangle$ and $|\mathbf{pg}\rangle$, and denote by $a^{\mathbf{ne}}(\mathbf{k}_n\nu)$ and $a_{\mathbf{pg}}(\mathbf{k}_p\pi)$ linear combinations of the wave functions of the zone electrons and holes, chosen to form an orthonormal system and to depend analytically on \mathbf{k}_n and \mathbf{k}_p ; in all other respects the choice of these functions is thus far arbitrary. We expand the wave function of the exciton in a series

$$a_{\mathbf{pg}}^{\mathbf{ne}} = \sum_{\mathbf{k}_n\mathbf{k}_p\nu\pi} C_{\mathbf{k}_p\pi}^{\mathbf{k}_n\nu} a^{\mathbf{ne}}(\mathbf{k}_n\nu) a_{\mathbf{pg}}(\mathbf{k}_p\pi) \quad (10)$$

and construct the functions

$$b_{\rho\pi}^{\mathbf{nv}} = \frac{1}{N} \sum_{\mathbf{k}_n\mathbf{k}_p} C_{\mathbf{k}_p\pi}^{\mathbf{k}_n\nu} \exp\{i(\mathbf{n}\mathbf{k}_n + \mathbf{p}\mathbf{k}_p)\}. \quad (11)$$

We can then show that (2) is transformed into

$$\begin{aligned} E[\{b_{\rho\pi}^{\mathbf{nv}}\}] &= \sum_{\mathbf{n}\mathbf{p}\nu\nu'\pi} \bar{b}_{\rho\pi}^{\mathbf{nv}} H^{\nu\nu'} \left(\frac{1}{i}\nabla_n\right) b_{\rho\pi}^{\mathbf{nv}'} \\ &+ \sum_{\mathbf{n}\mathbf{p}\nu\pi\pi'} \bar{b}_{\rho\pi}^{\mathbf{nv}} H_{\pi\pi'} \left(\frac{1}{i}\nabla_p\right) b_{\rho\pi'}^{\mathbf{nv}'} \\ &- \sum_{\mathbf{n}\mathbf{p}} \frac{e^2}{|\mathbf{n}-\mathbf{p}|} \sum_{\nu\nu'\pi'\pi} \overline{a^e\left(\frac{1}{i}\nabla_n, \nu\right) a_g\left(\frac{1}{i}\nabla_p, \pi\right) b_{\rho\pi}^{\mathbf{nv}}} \\ &\times a^e\left(\frac{1}{i}\nabla_n, \nu'\right) a_g\left(\frac{1}{i}\nabla_p, \pi'\right) b_{\rho\pi'}^{\mathbf{nv}'} \\ &+ \sum_{\mathbf{n}\mathbf{p}\mathbf{n}'\mathbf{p}'\nu\pi\nu'\pi'} U_{\mathbf{p}\mathbf{p}'} \left\{ \overline{x_{\mathbf{p}\pi, i}^{\mathbf{nv}} \left(\frac{1}{i}\nabla_n, \frac{1}{i}\nabla_p\right) b_{\rho\pi}^{\mathbf{nv}}}, \dots \right. \\ &\left. \dots \left| x_{\mathbf{p}'\pi', i}^{\mathbf{n}'\nu'} \left(\frac{1}{i}\nabla_{n'}, \frac{1}{i}\nabla_{p'}\right) b_{\rho\pi'}^{\mathbf{n}'\nu'} \dots \right\}, \quad (12) \end{aligned}$$

where

$$H^{\nu\nu'}(\mathbf{k}_n) = \sum_{e e'} \overline{a^e(\mathbf{k}_n\nu)} H^{ee'}(\mathbf{k}_n) a^{e'}(\mathbf{k}_n\nu'), \quad (13)$$

$$H_{\pi\pi'}(\mathbf{k}_p) = \sum_{g g'} \overline{a_g(\mathbf{k}_p\pi)} H_{g g'}(\mathbf{k}_p) a_{g'}(\mathbf{k}_p\pi'), \quad (14)$$

$$x_{\mathbf{p}\pi, i}^{\mathbf{nv}}(\mathbf{k}_n\mathbf{k}_p) = \sum_{e g} x_{\mathbf{p}g, i}^{\mathbf{ne}} a^e(\mathbf{k}_n\nu) a_g(\mathbf{k}_p\pi) \text{ etc.} \quad (15)$$

$$a^e(\mathbf{k}_n\nu) = \sqrt{N} a^{\mathbf{ne}}(\mathbf{k}_n\nu) e^{-i\mathbf{k}_n\mathbf{n}},$$

$$a_g(\mathbf{k}_p\pi) = \sqrt{N} a_{\mathbf{pg}}(\mathbf{k}_p\pi) e^{-i\mathbf{k}_p\mathbf{p}}; \quad (16)$$

the differentiation operators that enter as arguments into the functions a^e , a_g , $x_{\mathbf{p}g, i}^{\mathbf{ne}}$ etc. act only on the function $b_{\mathbf{p}g}^{\mathbf{nv}}$.

Relation (12) is the principal formula, from which the transition to the macroscopic theory should be carried out in the various cases.

Let us consider one example. It follows from (9) that the greatest interest, from the point of view of the influence of the resonance mechanism, attaches to the investigation of the structure of the exciton zone near the point $\mathbf{k} = 0$; on the other hand, in the effective-mass approximation, which we use here, we can describe only the states near the bottom of the exciton zone. We shall therefore assume that as we neglect the resonance interactions the minimum of the exciton zone is located at the point $\mathbf{k} = 0$.

Let us denote by \mathbf{k}_n^0 and \mathbf{k}_p^0 the position of the bottom of the lowest electron zone E^0 , and the top of the highest hole zone E_0 . At the points \mathbf{k}_n^0 and \mathbf{k}_p^0 , generally speaking, contact between several zones can take place. The functions $a^{\mathbf{ne}}(\mathbf{k}_n\nu)$ are conveniently chosen such that some (the functions of the first group) belong to the linear envelope of the wave functions of the electron bands that make contact at the point of absolute minimum, and the others (functions of the second group) belong to its orthogonal complement. Analogously, we choose and break up into two groups the functions $a_{\mathbf{pg}}(\mathbf{k}_p\pi)$. If the radius of the exciton is sufficiently large, the predominant role in the expansion (10) is assumed by the functions of the first group, and the functions of the second group can be neglected. Henceforth the sums that extend only over the functions of the first group will be designated by primes.

The bottom of the exciton zone is located at the point $\mathbf{k} = 0$, only if the vectors $\mathbf{k} = \mathbf{k}_n^0 + \mathbf{k}_p^0$ and $\mathbf{k} = 0$ are equivalent. This can occur actually only when the bottom of the electron zone and the ceiling of the hole zone (or of an entire group of zones) are located at the center of the Brillouin zone ($\mathbf{k}_0 = \mathbf{k}_n^0 = \mathbf{k}_p^0 = 0$), or at one of the symmetry points on its surface ($\mathbf{k}_0 = \mathbf{k}_n^0, \mathbf{k}_p^0$). In the latter case we shall assume for simplicity that this point of the extremum is unique, i.e., that all the points to which it goes under the operation of the factor group and the operation of time reversals are equivalent to it.

Introducing the smoothed functions

$$B_{\pi}^{\nu}(n, \mathbf{p}) = \frac{1}{v} b_{\rho\pi}^{\mathbf{nv}} \exp\{-i\mathbf{k}_0(\mathbf{n} + \mathbf{p})\},$$

assuming that the zone-zone transitions at the point \mathbf{k}_0 are allowed, and confining ourselves in

the resonance terms to terms of zero order in \mathbf{k} , we obtain, after varying over $B_{\pi}^{\nu}(\mathbf{n}, \mathbf{p})$ in the usual effective-mass approximation

$$\begin{aligned}
 & - \sum_{\nu'} D_{ij}^{\nu'} \nabla_{ni} \nabla_{nj} B_{\pi}^{\nu'}(\mathbf{n}, \mathbf{p}) - \sum_{\pi'} D_{\pi\pi', ij} \nabla_{pi} \nabla_{pj} B_{\pi'}^{\nu}(\mathbf{n}, \mathbf{p}) \\
 & - \frac{e^2}{|\mathbf{n}-\mathbf{p}|} B_{\pi}^{\nu}(\mathbf{n}, \mathbf{p}) + \sum_{\nu\pi'} \int d\mathbf{n}' d\mathbf{p}' \delta(\mathbf{n}-\mathbf{p}) \\
 & \times \left[\overline{(r_{\pi}^{\nu}(\mathbf{k}_0), \nabla_{\mathbf{p}})} (r_{\pi'}^{\nu'}(\mathbf{k}_0), \nabla_{\mathbf{p}'}) \frac{e^2}{|\mathbf{p}-\mathbf{p}'|} \right] \\
 & \times \delta(\mathbf{n}'-\mathbf{p}') B_{\pi'}^{\nu'}(\mathbf{n}', \mathbf{p}') = \varepsilon B_{\pi}^{\nu}(\mathbf{n}, \mathbf{p}), \quad (17)
 \end{aligned}$$

where

$$r_{\pi}^{\nu}(\mathbf{k}_0) = \sum_{\mathbf{n}} r_{\rho\pi}^{\nu\mathbf{n}}(\mathbf{k}_0, \mathbf{k}_0) \exp\{i\mathbf{k}_0(\mathbf{n}-\mathbf{p})\}, \quad \varepsilon = E - (E^0 - E_0).$$

The first three terms of the left half coincide with the Hamiltonian considered in reference 10. The coefficients $D_{ij}^{\nu\nu'}$ and $D_{\pi\pi', ij}$ determine the structure of the electron and hole zones near the extrema. The connection between the various coefficients, which follows from the symmetry of the crystal, can be found by group-theoretical methods.^{11,12} The last term is due to resonance interactions. Thus, introducing resonant interactions into the theory in the approximation considered here leads to the appearance of a characteristic contact term and to the transformation of the differential equation into an integro-differential one.

To solve the equations of (17), which have the form of plane waves with quasi-momentum \mathbf{k} , we have $B_{\pi}^{\nu}(\mathbf{p}, \mathbf{p}) = B_{\pi}^{\nu}(0, 0) \exp(i\mathbf{k}\mathbf{p})$ and the contact term assumes the form

$$\frac{4\pi e^2}{k^2} \sum_{\nu\pi'} \overline{(r_{\pi}^{\nu}(\mathbf{k}_0), \mathbf{k})} (r_{\pi'}^{\nu'}(\mathbf{k}_0), \mathbf{k}) B_{\pi'}^{\nu'}(\mathbf{n}, \mathbf{p}) \delta(\mathbf{n}-\mathbf{p}). \quad (18)$$

Although the mean value of the contact term is proportional to $(r_0/r_{\text{exz}})^3$, where r_0 and r_{exz} are respectively quantities on the order of the dimensions of the elementary cell and of the radius of the exciton state, this term should be retained, since it is connected directly with the macroscopic characteristic (the oscillator strength for a tran-

sition into the exciton state), and leads to a qualitative change in the law of dispersion near the point $\mathbf{k} = 0$. In addition, the resonance term may split the degenerate levels.

An investigation of the higher terms of the expansion in powers of \mathbf{k} in resonance terms and the formulation of a law of dispersion in crystals with a different symmetry are outside the scope of this communication.

For triplet states in a system of equations analogous to (1), there are no terms of the resonance type,^{13,6} and consequently the usual form of this theory still applies to them.

The author is grateful to S. I. Pekar for an evaluation of this work.

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Translated by J. G. Adashko