POSSIBLE STATES OF QUASI-UNIDIMENSIONAL SYSTEMS

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It is shown that a quasi-unidimensional system can exist in three states: ordinary metal, superconductor, and antiferromagnetic dielectric. The antiferromagnetic state exists only when the number of electrons in the elementary cell is exactly equal to unity. It is found what relations between the interaction constants lead to one or another state. A comparison is made with the results for exactly solvable models. Corrections to the magnetic susceptibility are calculated; they depend logarithmically on the temperature or the magnetic field.

1. INTRODUCTION

In recent years there have been investigated experimentally a number of substances that possess a thread-like structure. Examples are substances containing TCNQ. In these substances the molecules form threads separated by comparatively large distances; this allows us, in first approximation, to consider the threads independently. Such quasi-unidimensional systems should in principle possess a number of interesting properties. Depending on the number of electrons per molecule and on the interaction between them, the quasi-unidimensional systems may be metals, dielectrics, superconductors, or antiferromagnets.

In a theoretical study of unidimensional electronic systems, there are several approaches. In some special cases (the Hubbard model and a gas with a delta-shaped potential of interaction) exact solutions can be found. From the exact solutions it is comparatively simple to extract the energy of the ground state and the spectrum of certain excitations. So far, however, nobody has succeeded in giving a definitive judgment regarding the character of the ground state; that is, is the system a metal, a superconductor, a dielectric, etc.? On the other hand, one can arrive at conclusions about the character of the ground state by using various approximate methods. There is of course a possibility that such conclusions may be wrong; therefore it is very useful if one can find a way to compare the various results of approximate and exact theories. One such approximate solution was found in [1], where it was shown that in the presence of repulsion, an electron gas retains the properties of a normal metal. In the case of attraction, in the parquet approximation, a pole was obtained in the scattering amplitude. This pole does not indicate a phase transition at finite temperatures; this cannot occur in unidimensional systems. The appearance of a pole leads only to the result that at low temperatures, the interaction becomes strong; therefore the parquet approximation is inapplicable, and the properties of the system may change greatly. The comparison carried out below with the exact solution of Gaudin shows that in this case there is a gap in the single-electron spectrum.

Reference [1] took no account of the periodic potential of the lattice. It is shown below that the transfer processes arising because of this potential may lead to a qualitative change of the picture. In the case of a weak bare interaction, the form of the ground state is determined by the relations among three constants that describe the bare interaction. When, for example, the relations between the constants correspond to the Hubbard model, the state possesses superconducting properties in the case of attraction and antiferromagnetic in the case of repulsion. When there is another relation between the constants, a state may be obtained that is similar to that of a normal metal at all temperatures.

In this last case, and for not too low temperatures in the remaining cases also, an expression is obtained for the paramagnetic spin susceptibility and for the other generalized susceptibilities.

2. EXACTLY SOLVABLE MODELS

At present there are known some exactly solvable unidimensional models of interacting Fermi particles. These are the case of a gas with a delta-function interaction (Gaudin [2], Yang [3]) and the so-called Hubbard model (Lieb and Wu [4]).

In the case of a gas with delta-function interaction, the Hamiltonian of the system has the form

\[ H = -\frac{1}{2} \sum_j \frac{\partial^2}{\partial x_j^2} + t \sum_{\langle i,j \rangle} \delta(x_i - x_j). \]  

The unidimensionality of the system allows us to use for the solution of the problem a method first introduced by Bethe [5] for finding the spectrum of a unidimensional spin system. Such a program was carried out by Gaudin [2] and by Yang [3]. There were obtained as a result systems of integral equations, which determined the energy of the ground state and of the excited states and the wave functions. The form of the wave functions is determined by solutions of the same integral equations.

Unfortunately the systems of integral equations are very complicated even for the ground state. Furthermore, their number increases when we go over to many-particle excitations. So far, the equations have been integrated numerically only for the ground state and for several types of single-particle excitations.

The solutions have the simplest form in the strong-
coupling limit. For strong attraction, the energy of the ground state is

$$E = -\frac{1}{4}g^2(N/2 - S),$$

(2)

where $N$ is the total number of electrons and $S$ is the total spin. The form of this solution corresponds to the fact that electrons with opposite spins form spins with coupling energy $g^2/4$, which gives the chief contribution to the total energy. The state of minimum energy is that with total spin zero. The susceptibility is also zero as long as the magnitude of the magnetic field is less than the critical value $H_c = g^2/\mu_B$.

If the number of electrons is odd, the minimum value of the total spin is $S/2$; therefore the energy of the ground state of an odd number of particles is on the average larger than of an even number. This difference is $\Delta E = g^2/8$ and constitutes a gap in the energy of single-particle excitations. We note that for an even number of particles, $2\Delta E$ coincides with $\mu_+ - \mu_-$, the difference of chemical potentials corresponding to increase and to decrease of the number of particles in the system by unity. As is well known, the nonvanishing of this difference is a characteristic property of dielectrics and superconductors. The magnitude of the gap has been found in the strong-coupling limit; but the energy is an analytic function of $g$ for finite $g$, and therefore it may be asserted that the gap in the single-particle spectrum exists for an arbitrary attraction.

For repulsion, the gap is absent. (The expression (2) for the energy is independent of the length of the chain and gives zero compressibility. The term of the next order in $g^{-1}$ is independent of $g$ and gives a compressibility 16 times smaller than in an ideal gas.)

In the model solved by Gaudin, there was no allowance for the periodic field of the lattice. The Hubbard model is the opposite limiting case. The Hamiltonian of the electrons in this model has the form

$$H = T \sum_{\langle i,j \rangle} c_i^\dagger c_j + J \sum_i c_i^\dagger c_i c_i c_i^\dagger,$$

(3)

where the sum is over the numbers of the molecules in the chain, and in the first term the sum is over nearest neighbors.

The exact solution of this model was found by Lieb and Wu[4]. For negative $J$, corresponding to attraction, the electrons, just as in the free-gas model, are joined in pairs. The gap in the single-particle spectrum can be found by two methods: from the magnitude of the minimum magnetic field necessary to break up the pairs, and from the difference $\mu_+ - \mu_-.

A surprising property of the Hubbard model is that when the number of electrons exactly coincides with the number of sites, it is possible to obtain a formula for the gap which is correct for arbitrary intensity of the interaction. The appropriate formulas were found in papers[5,6,7]. In the limit of small coupling $\mu_+ - \mu_-$ is equal to $TJ$. As in the case of a gas, this value coincides with the energy of coupling of a pair. Its difference from the value for a gas is due to the difference in the dependence of energy on momentum.

In the weak-coupling limit,

$$\mu_+ - \mu_- = 8\pi^{-1/2}TJ e^{-2\pi \sqrt{2}/g},$$

(4)

Except for the multiplier of the exponential, this expression coincides with that which is obtained for the coupling energy of a pair in the approximate theories (see[1] and below).

The surprising properties of the Hubbard model are not exhausted by this one. It turns out that $\mu_+ - \mu_-$ is different from zero also in the case of repulsion, if only the number of electrons is exactly equal to the number of sites. The gap in the single-particle spectrum disappears upon destruction of the exact equality of the number of electrons and the number of sites. The gap in the spectrum is determined as before by formula (4), but the susceptibility is different from zero even in zero field[7]. This shows that in the case of repulsion, the pairs have a spin equal to unity, and not to zero, as for attraction. Because the spin of the ground state is equal to zero, one can imagine that this state has antiferromagnetic character. The result concerning the antiferromagnetic character of the ground state in the Hubbard model with repulsion was obtained earlier[9] by means of the method of the self-consistent field; this method, however, does not always lead to results that are correct even qualitatively. For example, Overhauser[10, 11], by means of this method, obtained the result concerning the antiferromagnetic character of the ground state of a unidimensional free-electron gas with repulsion; this does not agree either with the results of the exact solution[2] or with the results of the parquet approximation[11]. It is shown below that the parquet approximation agrees qualitatively with the exact results in these cases.

3. A QUASI-UNIDIMENSIONAL CRYSTAL

A quasi-unidimensional crystal represents a lattice consisting of threads, the distances between which are large in comparison with the distance between molecules. Therefore it is possible in first approximation to neglect the tunnel penetration of an electron into neighboring threads, and to suppose that the electron moves in a potential which is a periodic function of the coordinate $x$, directed along the thread, and which increases in the transverse direction. In the simplest case, there is one molecule in one period. To each molecule belongs an integral number of electrons. In other cases the symmetry group of the potential $U$ contains a screw axis or a glide plane. Then there may correspond to each molecule a fractional number of electrons.

The wave function of the electrons, in the single-electron approximation, has the form $\psi(r) = \varphi(r) e^{i\text{ort}}$, where $\varphi(r)$ has the same symmetry as the potential $U$. The potential of interaction between electrons, $V(r_i, r_j)$, is some function of the difference of coordinates $r_i - r_j$ and is a periodic function of the sum, having the same symmetry as the function $U(r)$.

The case considered below is that in which the distance between molecules in the chain is small, and the interaction between electrons is smaller than the gap width. Then one can choose as zeroth approximation the free-electron approximation. If there are fewer than two electrons for each molecule, then the band is filled incompletely, and the chain possesses metallic properties. Even a weak interaction, however, can change these properties. In fact, as was shown in[13],

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upon lowering of the temperatures the corrections to the Born approximation for the scattering amplitude increase logarithmically, and the effective interactions may become strong. The logarithmically large corrections arise from electrons with quasimomenta close to the Born approximation for the scattering amplitude. Upon lowering of the temperatures the corrections to increase logarithmically, and the effective interactions may become strong. The logarithmically large corrections arise from electrons with quasimomenta close to the Born approximation for the scattering amplitude.

The last expression describes transfer processes in which the quasimomentum of two electrons changes by a quarter-period of the reciprocal lattice. Thus in the logarithmic approximation, allowance for the periodic field of the lattice reduces to allowance for transfer processes.

It is easily accomplished in a unidimensional system. The contradiction is due to the fact that the pole expressions for the amplitude at finite temperatures, which is impossible in a unidimensional system. The contradiction is due to the fact that the pole expressions for the amplitude.

3. In the logarithmic variables \( \xi = \ln \epsilon / \max (\Delta \epsilon, \nu \Delta p) \), where \( \Delta \epsilon \) is the energy to the Fermi surface; \( \Delta \epsilon \) and \( \nu \Delta p \) are supposed to be large in comparison with the temperature. It is convenient to write equation (6), choosing for independent effective interaction potentials \( \gamma_1, \gamma_2, \) and \( \gamma_3 \), corresponding to the priming potential (7). The scattering amplitudes with retention of the quasimomentum (7) and with change of the quasimomentum by \( 4pF \) (7') are

\[
\Gamma_{\text{sys}} = \gamma_1 \Delta \omega m_0 - \gamma_2 \Delta \omega m_0 = \frac{1}{2} \gamma_1 \Delta \omega m_0 - \frac{1}{2} \gamma_2 \Delta \omega m_0, \\
\Gamma_{\text{sys}} = \gamma_1 (\Delta \omega m_0 - \Delta \omega m_0),
\]

where

\[
\gamma_1 = \gamma_1 - 2 \nu, \quad \gamma(0) = g_1 = g_1 - 2g_2.
\]

As a result, equation (7) can be written in the form of a system of nonlinear integral equations

\[
\gamma(\xi) = g_1 - \int \gamma(\xi') d\eta, \quad \gamma_1 = \gamma_1 - \frac{\partial}{\partial \xi} (\gamma(\xi') d\eta),
\]

\[
\gamma(\xi) = g_1 - \int \gamma(\xi - \xi') d\eta. \quad \gamma_1 = \gamma_1 - \frac{\partial}{\partial \xi} (\gamma(\xi - \xi') d\eta).
\]

In the derivation of this equation, the cutting off of all the logarithmic integrals was done at energies of order \( \epsilon_F \). It is to be expected that the interaction (7) includes exchange of phonons and the Little mechanism of inter­

acting by excitation of electronic levels. Therefore the constants \( g_1, g_2, \) and \( g_3 \) are not constant over the whole energy range, but change at energies of the order of the Debye frequency or of low-lying electronic levels. Such a change can be allowed for by renormalization of the constants \( g \). The renormalization may be appreciable if the constants \( g \) are not very small, and it is easily accomplished in each specific case. After differentiation, the system (8) takes the form

\[
\gamma' = -\gamma', \quad \gamma'' = -\gamma', \quad \gamma'' = -\gamma \nu_\gamma.
\]

The solution of the first equation is determined by the constant \( g_1 \) alone:

\[
\gamma_1 = g_1 / (1 + g_1 \xi).
\]

The form of the solution of the second and third equations depends importantly on the relation between the constants \( g_2 \) and \( g_3 \). With the notation \( |g_2^2 - g_3^2| = D^2 \), we get

\[
\gamma_1 = \pm \gamma_1 = g_1 / (1 + g_1 \xi) \quad \text{when} \quad g_1 = g_1^*;
\]

\[
\gamma_1 = -D \cosh D(\xi - \xi'), \quad \gamma_1 = \pm D \cosh D(\xi - \xi'), \quad \text{when} \quad g_1 > g_1^*;
\]

\[
\gamma_1 = -D \cosh D(\xi - \xi'), \quad \gamma_1 = \pm D \cosh D(\xi - \xi'), \quad \text{when} \quad g_1 < g_1^*.
\]

For \( g_3 = 0 \) we get \( \gamma_3 = 0 \), but \( \gamma_4 \) coincides with its priming value \( g_4 \).

The expression (10) for the amplitude \( \gamma_1 \) does or does not have poles, depending on the sign of \( g_1 \). If there is one electron per molecule in the unidimensional chain, then \( g_3 = 0 \); poles may occur also in the amplitudes \( \gamma_3 \) and \( \gamma_4 \). For example, in the Hubbard model \( g_1 = g_2 = g_3 = -g_4 = g_4 \), and, depending on the sign of \( g_4 \), a pole may occur either in the amplitude \( \gamma_1 \) or in \( \gamma_3 \) and \( \gamma_4 \). A pole in the scattering amplitude would indicate instability of the system and a phase transition at finite temperatures, which is impossible in a unidimensional system. The contradiction is due to the fact that the pole expressions for the amplitude were obtained in the parquet approximation. This ap-
proximation is applicable only in the range of temperatures, energies, and momenta in which the effective interaction is small; that is, \( \gamma \ll 1 \). Therefore when the relations among the constants are such that the amplitudes have no poles, the interaction remains weak, and the system should retain metallic properties. In particular, the spectrum of single-particle excitations should remain gapless. A pole in the expressions for the amplitudes means only that at sufficiently low temperature, the interactions between the electrons become strong. On reaching order of magnitude unity, the amplitudes \( \gamma \) themselves limit their own growth. At finite temperatures, no singularities should occur, but the state at zero temperature may be ordered and may have a gap in the single-particle spectrum. Comparison with the exactly solved models supports this supposition. As was mentioned above, in the solution of Gaudin\[2\] the gap in the single-particle spectrum occurs only for attraction, whereas in the solution of Lieb and Wu\[4\] for the Hubbard model it occurs for arbitrary sign of the interaction.

Thus although the question of the existence and character of order at zero temperature cannot be solved within the framework of the parquet approximation, this approximation allows us to express nonrigorous ideas about the symmetry of the ground state. We place the system in a weak generalized external field of one or another symmetry, and we explain for what symmetry of the field there occurs a strong change of the Green functions. These changes are described by vertices, the equation for which, in the parquet approximation, are represented graphically in the form

\[
\begin{align*}
\Delta(z) &= \frac{1}{2} \int \left[ y_i(n) + y_i(n) \right] \Delta(n) d\eta. \\
\end{align*}
\]

In the derivation of this equation, as in the derivation of equation (6) for the amplitudes, the method of Suda-kov was used. Here it was assumed that all the momenta that entered had a single order of magnitude and, in logarithmic variables, coincided. The explicit form of the equation depends on the symmetry of the field. If the external field generates a pair of particles and contributes to superconducting coupling, then the equation for the corresponding vertex function \( \Delta \) is expressed as follows in terms of the amplitudes:

\[
\Delta(z) = \frac{1}{2} \int \left[ y_i(n) + y_i(n) \right] \Delta(n) d\eta. 
\]

On expressing \( \gamma_2 \) in terms of \( \gamma_4 \) by formula (7'), differentiating with respect to \( \xi \), and solving the linear equation obtained, we get

\[
\Delta(z) = \exp \left\{ -\frac{1}{4} \int \left( \partial y_i - y_i \right) d\eta \right\}. 
\]

In analogous manner, a field with period 2pF, acting on the spins and leading to antiferromagnetic order, leads to a vertex \( \sigma \) equal to

\[
\sigma(z) = \exp \left\{ \frac{1}{4} \int \left( y_i - y_i \right) d\eta \right\}. 
\]

The vertex \( n(\xi) \), which arises from a periodic external field, acting on the density and leading to a doubling of the period, is equal to

\[
n(\xi) = \exp \left\{ \frac{1}{4} \int \left( y_i + y_i \right) d\eta \right\}. 
\]

The integrals that occur in formulas (13)–(15), after substitution in them of the amplitudes (10) and (11), can be calculated in explicit form for an arbitrary relation between the constants \( g_3 \) and \( g_4 \). But in order to find the possible types of ordering, it is sufficient to know that singularities of the functions \( \Delta, \sigma, \) and \( n \), which are determined by the poles of the functions \( \gamma \), located at the points \( \xi = -g_1 \) and \( \xi = \xi_0 \). As distinguished from the positions of the singularities, their form does not depend on the relation between the constants of the priming interaction, but is determined entirely by the residues at the poles of the functions \( \gamma \).

As a result, we get for the singular parts

\[
\Delta = \frac{(1 - \frac{1}{2} \rho_0)^{\mu}}{(1 + \frac{1}{2} \rho_0)^{\nu}}, \quad \sigma = \frac{(1 + \frac{1}{2} \rho_0)^{\mu}}{(1 - \frac{1}{2} \rho_0)^{\nu}}, \quad n = \frac{(1 + \frac{1}{2} \rho_0)^{\mu}}{(1 - \frac{1}{2} \rho_0)^{\nu}}.
\]

The generalized susceptibilities, which describe the response of the system to the respective fields, in the parquet approximation, are determined by the graph

\[
\Pi_{\alpha} = \frac{(1 - \frac{1}{2} \rho_0)^{\mu}}{(1 + \frac{1}{2} \rho_0)^{\nu}}, \quad \Pi_{\alpha} = \frac{(1 + \frac{1}{2} \rho_0)^{\mu}}{(1 - \frac{1}{2} \rho_0)^{\nu}}.
\]

The last expression, for example, describes the behavior of the phonon Green function for phonon momenta close to 2pF. Note that the expression given in\[15\] contains an incorrect exponent of the singularity.

Just as in the case of poles, in the amplitudes a going to infinity of the susceptibility indicates an instability of the system with respect to the occurrence of ordering of the corresponding symmetry. Although it follows from formula (17) that this instability occurs at finite temperatures, nevertheless, here also, because of the inapplicability of the parquet approximation close to the poles of the amplitudes \( \gamma \), it is possible to draw only the conclusion that for low temperatures the vertices and the generalized susceptibilities can become anomalously large. One may suppose that at zero temperature ordering of a definite symmetry occurs only in case the corresponding vertex and susceptibility increase.

Therefore superconducting coupling occurs only when there is a pole in the amplitude \( \gamma_2 \) at the point \( \xi = -g_1 \); that is, for negative \( g_1 \). Similarly, an antiferromagnetic state can occur only when there are poles in the amplitudes \( \gamma_3 \) and \( \gamma_4 \), and it is not sensitive to a pole in the amplitude \( \gamma_1 \). Doubling of the period can occur in both cases. From the parquet approximation it is impossible to elucidate, for example, whether, in the case of a pole in \( \gamma_1 \), there will be simultaneously both superconducting coupling and a doubling of the period, or one or the other. For definiteness, we shall call this state superconducting. When the
relations among the constants are such that there are poles both in $\gamma_1$ and in $\gamma_4$. Evidently, that pole will be decisive which is located at the smaller values of $\xi$.

Thus the symmetry of the state at zero temperature is determined by the relations among the priming constants of the interaction (see figure). For example, when $g_1 > 0$ and $g_4 > |g_3|$, the amplitudes have no poles, and will approach zero logarithmically at low temperatures and energies. (The situation is analogous to zero charge in the quantum electrodynamics.) In this case, the formulas (10) and (11) are applicable at all temperatures, the interaction always remains weak, and the state does not differ essentially from the state of a free electron gas. In the remaining cases, a gap may occur in the spectrum of electronic excitations.

In the parquet approximation, the size of the gap is determined by solving the homogeneous equation corresponding to equation (12); that is, from the condition that the solutions of (13), (14), and (15) become infinite. Hence we get for the magnitude of the gap $\Delta \xi$ for negative $g_1$ and $\xi_0$

$$\Delta \xi = \psi_0 \exp \left( -\frac{1}{|g_1|} \right) \text{ or } \Delta \xi = \psi_0 \exp \left( -\frac{1}{|g_4|} \right).$$

(18)

In the Hubbard model, these results agree with the results of the exact solution except for a pre-exponential multiplier equal to $\sqrt{|g|}$.

One may imagine that the gap in the spectrum indicates the appearance of long-range order at zero temperature. In real quasi-unidimensional systems, the tunnelling penetration of the electrons into neighboring sites will lead in these cases to the existence of an ordered state even at finite temperatures.

In the parquet approximation, it is possible to find corrections to the heat capacity and the susceptibility. In the zeroth approximation with respect to the interaction, we obtain the usual expressions. The corrections of first order contain no logarithmic divergences; in the following orders, the degree of the logarithm is at least one less than the degree of the interaction. Therefore everywhere where the parquet approximation is applicable, the corrections to the susceptibility and the heat capacity are small. These corrections, however, in contrast to the principal term, have a temperature dependence and are consequently of some interest. In the first order with respect to the effective interaction $g_1$, the corrections to the susceptibility arise both from the vertices and from complications of the Green functions. In the first order with respect to the interaction, the change of the Green function reduces to a renormalization of the electron speed. Therefore in the first order with respect to the effective interaction, there are in the heat capacity no terms logarithmically dependent on temperature.

For calculation of the corrections to the susceptibility, we note that for weak interaction between the electrons, the Green function has the form

$$G = a / [e - v(p - p_F)].$$

(19)

The renormalized multiplier $a$ depends logarithmically on $\xi$, but one can show that its effect on the susceptibility is counteracted by a contribution from regions far from the Fermi surface. For this purpose we note that in a homogeneous low-frequency magnetic field, the change of the Green function is

$$\Delta G_{\omega, \nu} = \frac{\partial G}{\partial \nu} \chi.$$  

(20)

Such a field does not produce physical changes, and the susceptibility in it is zero.

After the transformations that are usual in the theory of a Fermi fluid, for an arbitrary relation between $k$ and $\omega$, we obtain for the susceptibility the expression

$$\chi = \int \frac{d\nu}{\nu} \frac{\partial G^\dagger}{\partial \nu} \left[ G - [G]_{\nu} \right] \frac{1 + \Gamma(GG^\dagger - [G]_{\nu})}{\partial \nu} \left[ \frac{\partial G^\dagger}{\partial \nu} \right].$$

(21)

Here the integration is carried out only over the region close to the Fermi surface, where one may use expression (19) for the Green function. The contribution from the first term in the square brackets leads to the Pauli susceptibility with an effective mass. The renormalized multiplier $a$ in this term is canceled. In the second term, which is a small correction, it may be neglected. On substituting for the amplitude $\Gamma$ the expression obtained above, we get the static susceptibility

$$\chi = \chi_0 \left[ 1 + \frac{1}{2} \ln \left( 1 + \frac{\nu F}{\max \{e, \nu H\}} \right) \right].$$

(22)

In the region of a normal metal, the formula obtained is applicable at as small fields and temperatures as is desired, and it implies a slow decrease of the susceptibility with decrease of temperature. In the superconducting and antiferromagnetic regions, the expression obtained is applicable only for sufficiently high temperatures, where the effective interaction is small. With further decrease of temperature, as is seen from the exact solutions, the drop becomes more rapid.

CONCLUSION

The basic result of the research is the assertion that, depending on the form of the interaction between the electrons, a quasi-unidimensional system may be in any of three states: metallic, superconducting, or antiferromagnetic. One may suppose that this assertion is correct for arbitrary strength of the interaction. All of the formulas that we have written down, however, are correct only for weak interaction. It is especially necessary to keep this in mind in comparing expression (22) for the magnetic susceptibility with experiment. Such a comparison is made difficult by the fact that the width of the band and the interaction between
the electrons are usually unknown. Experimentally\textsuperscript{[10]}, an increase of susceptibility with lowering of temperature has been observed. Apparently this indicates that in the substances studied, the interaction is not weak. The authors are grateful to A. A. Ovchinnikov and G. V. Ulmin for valuable comments.

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