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Dependence of the NMR relaxation time on the magnetic field in quasi-one-dimensional and quasi-two-dimensional crystals

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The effect of electron transitions between chains on the dependence of the NMR relaxation rate T_1^{-1} on the magnetic field H in highly conducting quasi-one-dimensional compounds is considered. It is shown that the study of this dependence is an effective method for determining the transverse resonance integrals in quasi-one-dimensional compounds. The dependence of T_1^{-1} on H in donor-acceptor crystals of the TTF-TCNQ and HMTTF-TCNQ type is found. The transverse resonance integrals in TTF-TCNQ are determined from data for the NMR relaxation. The experimentally observed logarithmic dependence of the NMR relaxation rate on the magnetic field in the compound HMTSF-TCNQ is explained. The dependence of the relaxation rate on the magnetic field in quasi-two-dimensional compounds is found.

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1. INTRODUCTION

Experimental studies of the NMR relaxation in highly conducting quasi-one-dimensional crystals of the TTF-TCNQ type[1-4] show that, at room temperatures and in sufficiently strong magnetic fields (10–40 kOe), the dependence of the NMR relaxation rate T_1^{-1} on the magnetic field H is observed to be of the form $T_1^{-1} \sim H^{-1/2}$ characteristic for one-dimensional systems. The increase of the quantity T_1^{-1} with decrease of H breaks down in fields below about 10 kOe, and T_1^{-1} tends to a constant limit as $H \to 0$. At the same time, the theory of NMR relaxation in metals shows that, when scattering of electrons by impurities or phonons is disregarded, the quantity T_1^{-1} in systems of any dimensionality is independent of the magnetic field H so long as the Zeeman energy $\hbar\omega_e$ of the electrons remains small compared with their Fermi energy ε_F. The latter condition is fulfilled by a large margin in the quasi-one-dimensional crystals investigated in Refs. 1–4. In connection with this it was noted in Ref. 1 that the dependence $T_1^{-1} \sim H^{-1/2}$ in quasi-one-dimensional crystals may be associated with nuclear-spin relaxation via the electron

system in conditions of strong scattering of electrons moving along the chain. In this situation the spectrum of the long-wavelength electron spin excitations responsible for the NMR relaxation via the electron system acquires a diffusive character: $\omega(k) = Dk^2$, where D is the coefficient of diffusion of the electrons along the chain. When the motion of the spin excitations has a diffusive character the spin density at a given site decreases with time t like $t^{-1/2}$, t^{-1}, and $t^{-3/2}$ as $t \to \infty$ in systems with dimensionaltiy 1, 2 and 3, respectively. This decay gives dependences of the rate of diffusion of the excitations on the frequency ω_e of the form $\omega_e^{-1/2}$, $|\ln\omega_e|$, and const as $\omega_e \to 0$ for systems with dimensionality 1, 2, and 3.[1)]

It has also been noted[1] that the limitation of the relaxation rate as $H \to 0$ in quasi-one-dimensional metals is connected with the effects of the three-dimensional motion of the electron spin excitations, i.e., with transitions of electrons from filament to filament (in layer crystals the limitation of the increase as $H \to 0$ is connected with transitions of electrons between layers).[2)]

Since the value of the relaxation rate as $H \to 0$ in strongly anisotropic crystals depends in an essential way on the transverse resonance integrals describing the motion of the electrons between the filaments (or layers), a study of the dependence of the NMR relaxation rate on the magnetic field gives the possibility of determining these integrals and thereby establishing the transverse structure of the electron spectrum of the crystals.

In principle, direct information on the width of the energy bands in the perpendicular (to the chains or layers) direction might be given by measurements of the transverse electrical conductivity of the metals. However, an estimate of the absolute value of the transverse resonance integrals from conductivity data is scarcely reliable in conditions when the anisotropy is very large (because of macroscopic defects and difficulties with contacts in direct-current measurements). In view of this, it appears to us to be more reliable to determine the transverse resonance integrals from data on the dependence of T_1^{-1} on H, since such measurements give information on the internal anisotropy intrinsic to the crystals.

To describe the three-dimensional motion of the electron spin excitations the authors of Ref. 1 introduced a phenomenological parameter $\tau_\perp^{-1}$—the frequency of electron hops between chains, and estimated it from the experimental data for $T_1^{-1}(H)$. This procedure is simple and physically visualizable, but only qualitatively reflects the essence of the dependence of T_1^{-1} on the transverse resonance integrals in weak magnetic fields. Therefore, the aim of the present work is to obtain the exact dependence of $T_1^{-1}(H)$ on the microscopic characteristics of quasi-one-dimensional and layer crystals. A knowledge of this dependence makes it possible to determine quantitatively the characteristics of the electron spectrum of quasi-one-dimensional and layer crystals for the transverse directions of motion of the electrons from experimental data on the dependence of the relaxation rate on the magnetic field.

2. FORMULATION OF THE PROBLEM AND BASIC EQUATONS

We shall consider that part of the nuclear relaxation rate of a nucleus with coordinate n which is determined by the isotropic (contact) hyperfine electron-nuclear interaction $A I_n S_n$, where I_n is the nuclear spin and S_n the electron spin on molecule n (to describe the motion of the electrons we shall use the tight-binding approximation). In a magnetic field the rate of relaxation as a result of this interaction for $\hbar\omega_e \ll T$ is determined by the expression

$$T_1^{-1} = \frac{2TA^2}{g^2\mu_B^2\omega_e} \operatorname{Im}\chi(n, \omega_e),\qquad (1)$$

where A is the hyperfine-structure constant and $\chi(n, \omega_e)$ is the local susceptibility of the electron system, without a magnetic field, for the site n at frequency ω_e.[7] If we take into account the anisotropic electron-nuclear dipolar interaction of the nucleus n with the spin of the molecule m, we obtain for T_1^{-1} an expression of the type

$$T_1^{-1} = \frac{T}{g^2\mu_B^2\omega_e}\left\{2A^2 \operatorname{Im}\chi(n, \omega_e) + \sum_m [b_{nm}^2 \operatorname{Im}\chi(m, \omega_e)\right.$$
$$\left. + C_{nm}^2 \operatorname{Im}\chi(m, \omega_n)]\right\},\qquad (2)$$

where $\omega_n = \gamma_n H$; γ_n is the nuclear gyromagnetic ratio. As will be shown below, the change in the law for the dependence of T_1^{-1} on the field occurs at frequencies $\omega_e \sim t_\perp^2\tau$, where τ is the mean scattering time and $t_\perp$ is the transverse resonance integral (in lower fields, T_1^{-1} ceases to depend on the magnetic field). Since $\omega_n \ll \omega_e$, the third term in the expression (2) is essentially independent of the field in the fields attainable in practice, and we shall not take into account below.

For crystals with one molecule in the unit cell the local susceptibility is the same for all molecules and the expression (2) takes the form (1) with a renormalized constant A. In donor-acceptor crystals with two conducting chains the local susceptibility is different for the different chains. In this case the expression (2) takes the form

$$T_{1\alpha}^{-1} = \frac{T}{g^2\mu_B^2\omega_e}\sum_{\beta=1,2} A_{\alpha\beta}^2 \operatorname{Im}\chi(n, \beta, \omega_e),\qquad (3)$$

where the indices $\alpha, \beta = 1, 2$ indicate the type of chain (acceptor or donor), n is the coordinate of the unit cell, $\chi(n, \alpha, \omega_e)$ is the local susceptibility of the chain of type α, which depends on α but is practically independent of n, the parameters $A_{\alpha\alpha}^2$ take into account the isotropic and anisotropic interaction of the nucleus at an α molecule with the spins of molecules of the same type α, and the parameters $A_{\alpha\beta}^2$ with $\alpha \neq \beta$ take into account the ansiotropic interaction of a nucleus of an α molecule with the spins of molecules of -type β.

For a system of free electrons, taking their scattering by impurities into account we have

$$\chi(n, \alpha; \omega_e) = -ig^2\mu_B^2 \int \frac{d\omega}{2\pi}\langle G(n\alpha, n\alpha; \omega) G(n\alpha, n\alpha; \omega+\omega_e)\rangle,\qquad (4)$$

where $G(n\alpha, m\beta; \omega)$ is the Green function of the motion of an electron from molecule $n\alpha$ to molecule $m\beta$ at frequency ω, and the symbol $\langle \ldots \rangle$ denotes averaging over the impurities.

Thus, with neglect of the Coulomb repulsion of the electrons the problem of the determination of T_1^{-1} reduces to averaging a product of Green functions over the impurities. For a three-dimensional isotropic system the corresponding calculations of the susceptibility were performed by Fulde and Luther, who calculated the average of the product of Green functions in the ladder approximation.[8] In the three-dimensional case the contribution of all the other diagrams is small in the parameter $(k_F l)^{-1}$, and the ladder approximation gives the solution of the problem for a system with a small quantity of impurities. In the present paper we also use this approximation, in an application to quasi-one-dimensional crystals, although it is known that in the one-dimensional case, generally speaking, all the other diagrams may not be small, even for $k_F l \gg 1$, because of specific interference effects in the scattering of an electron by impurities. Nevertheless, in the one-dimen-

A. I. Buzdin and L. N. Bulaevskiĭ   729

sional case too, situations in which the ladder approximation gives correct results are possible. For example, Gogolin, Mel'nikov, and Rashba have shown that in a one-dimensional system of electrons interacting with phonons and being scattered by impurities at not too low temperatures $T\tau_i \gg 1$ (where τ_i is the mean scattering time for scattering by impurities), in conditions of strong scattering by phonons ($\tau_{ph} \ll \tau_i$) and for a sufficiently large width Δ of the phonon spectrum ($\tau_i \Delta \gg 1$) the motion of the electrons is described by an ordinary kinetic equation that is equivalent to taking only the ladder sequence of diagrams into account.[9] In practice these conditions are fulfilled at room temperature in crystals with a sufficiently small quantity of impurities. At present we cannot estimate the parameter τ_i in the crystals under consideration, and so we do not know whether the conditions are fulfilled in them.[9] However, the use of the ladder approximation for $\omega_e \tau \ll 1$ (τ is the effective mean time of scattering of an electron by impurities and phonons) leads to diffusive character of the propagation of the spin excitations and to the dependence $T_1^{-1} \sim H^{-1/2}$, which is observed experimentally in TTF-TCNQ and NMP-TCNQ at room temperatures in magnetic fields above 10 kOe. In effect, these experimental results are a proof of the applicability of the ladder approximation for the crystals under consideration at those temperatures for which the dependence $T_1^{-1} \sim H^{-1/2}$ is observed in sufficiently strong fields H, although we do not now know with certainty which parameters determine the smallness of diagrams of the nonladder type in these conditions. Introducing the notation $G(n\alpha, m\beta, \omega) = G_{\alpha\beta}(n, m, \omega) \equiv G_{\alpha\beta}(n-m, \omega)$, we write the expression (4) in the form

$$\text{Im}\,\chi(n, \alpha; \omega_e) = -g^2\mu_B^2\,\text{Re}\int \langle G_{\alpha\alpha}(p+q, \omega)\,G_{\alpha\alpha}(p, \omega+\omega_e)\rangle \frac{dp}{(2\pi)^3}\frac{dq}{(2\pi)^3}\frac{d\omega}{2\pi}.$$

(5)

In the ladder approximation we obtain a system of equations for the average of two Green functions:

$$\langle G_{11}(p)G_{11}(p+q)\rangle = \langle G_{11}(p)\rangle\langle G_{11}(p+q)\rangle$$
$$+\frac{1}{2\pi\tau_1 N_1(0)}\langle G_{11}(p)\rangle\langle G_{11}(p+q)\rangle \int \langle G_{11}(p')G_{11}(p'+q)\rangle\frac{dp'}{(2\pi)^3}$$
$$+\frac{1}{2\pi\tau_2 N_2(0)}\langle G_{12}(p)\rangle\langle G_{12}(p+q)\rangle \int \langle G_{21}(p')G_{21}(p'+q)\rangle\frac{dp'}{(2\pi)^3}, \qquad (6a)$$

$$\langle G_{12}(p)G_{12}(p+q)\rangle = \langle G_{12}(p)\rangle\langle G_{12}(p+q)\rangle$$
$$+\frac{1}{2\pi\tau_1 N_1(0)}\langle G_{11}(p)\rangle\langle G_{11}(p+q)\rangle \int \langle G_{12}(p')G_{12}(p'+q)\rangle\frac{dp'}{(2\pi)^3}$$
$$+\frac{1}{2\pi\tau_2 N_2(0)}\langle G_{12}(p)\rangle\langle G_{12}(p+q)\rangle \int \langle G_{22}(p'+q)G_{22}(p')\rangle\frac{dp'}{(2\pi)^3}, \qquad (6b)$$

and analogous equations obtained from (6) by interchanging the indices $1 \rightarrow 2$. In Eqs. (6) τ_α is the effective mean free time of an electron on a chain of type α, and $N_\alpha(0) = 1/\pi v_\alpha$ and v_α are the density of states of electrons at the Fermi level and the Fermi velocity of the electrons of chain α (we consider the situation when the transverse resonance integrals are small and the contribution of the transverse motion of the electrons to the density of states $N_\alpha(0)$ is small). Introducing the notation

$$X_{\alpha\beta}(q, \omega, \omega_e) = \frac{1}{2\pi N_\alpha(0)}\int \langle G_{\alpha\beta}(p+q, \omega+\omega_e)G_{\alpha\beta}(p, \omega)\rangle\frac{dp}{(2\pi)^3},$$
$$X_{\alpha\beta}^0(q, \omega, \omega_e) = \frac{1}{2\pi N_\alpha(0)}\int \langle G_{\alpha\beta}(p+q, \omega+\omega_e)\rangle\langle G_{\alpha\beta}(p, \omega)\rangle\frac{dp}{(2\pi)^3},$$

(7)

we obtain from (6)

$$\text{Im}\,\chi(n, \alpha; \omega_e) = \chi_\alpha^0\,\text{Re}\int X_{\alpha\alpha}(q, \omega, \omega_e)\frac{dq}{(2\pi)^3}d\omega,$$

$$X_{11} = \frac{X_{11}^0(1-\tau_2^{-1}X_{22}^0)+\tau_2^{-1}X_{12}^0 X_{21}^0}{(1-\tau_1^{-1}X_{11}^0)(1-\tau_2^{-1}X_{22}^0)-\tau_1^{-1}\tau_2^{-1}X_{12}^0 X_{21}^0} \qquad (8)$$

and an expression for X_{22}, obtained from (8) for X_{11} by the interchange $1 \rightarrow 2$. In formula (8) the quantity χ_α^0 is the static susceptibility of a chain of type α. In calculating (7), (8) we make use of the conditions $T, \omega_e \ll \varepsilon_F$. Then in the calculation of the electron Green function the occupation numbers of the states can be taken at $T = 0$ (but the time τ_α corresponds to the temperatures under consideration!). Following Ref. 8, we divide the range of integration in the expression (8) for $\chi(n, \alpha, \omega_e)$ into three regions: 1) $\omega < -\omega_e$, 2) $-\omega_e < \omega < 0$, 3) $\omega > 0$. In the region 2 the quantity X_{11} depends in an essential way on ω_e, because of the opposite signs of the imaginary parts of the functions $\langle G \rangle$. Since $\omega \ll \varepsilon_F$, in this region we can put here $X_{11}(q, \omega, \omega_e) = X_{11}(q, 0, \omega_e)$. In the regions 1 and 3, because of the condition $\omega_e \ll \varepsilon_F$, we can put $\omega_e = 0$ and extend the integration over the region 2: the corresponding expression is found to be purely imaginary and does not give a contribution to T_1^{-1}. The expression (8) finally takes the form

$$\omega_e^{-1}\,\text{Im}\,\chi(n, \alpha; \omega_e) = \chi_\alpha^0\,\text{Re}\int X_{\alpha\alpha}(q, 0, \omega_e)\frac{dq}{(2\pi)^3}. \qquad (9)$$

We shall use the expression (9) afterwards, in the calculation of the quantity T_1^{-1} in quasi-one-dimensional and layer crystals. The further calculation of the quantity $\text{Im}\,\chi(n, \alpha, \omega_e)$ depends on the specific structure of the crystals. In the present article we shall consider quasi-one-dimensional crystals in which planes of acceptor (A) and donor (D) chains alternate (crystals with the TTF-TCNQ structure), and crystals in which donor and acceptor chains alternate in all the transverse directions (structure of the HMTTF-TCNQ type). For layer crystals the quantity T_1^{-1} will be calculated only for a structure with one layer in the unit cell.

3. RELAXATION IN QUASI-ONE-DIMENSIONAL CRYSTALS WITH STRUCTURE OF THE TIF-TCNQ TYPE

The structure of the TTF-TCNQ crystal in the plane perpendicular to the chains is shown schematically in Fig. 1; also shown there are transitions of electrons between atoms, described by the transverse resonance integrals t_{11}, t_{22}, and t_{12} (these are, respectively, the transitions between the nearest atoms of neighboring chains AA, DD, and AD). We denote by $\langle G_{\alpha\alpha}^0 \rangle$ the Green functions of the electrons in the layers α when transitions between chains of different kinds are not taken into account:

$$G_{\alpha\alpha}^0(p_z, p_x, \omega) = \left(\omega + \varepsilon_F - v_\alpha|p_z| - 2t_{\alpha\alpha}\cos p_x + \frac{1}{2\tau_\alpha}\text{sign}\,\omega\right)^{-1}, \qquad (10)$$

where p_z is the momentum along the chain and p_x is the momentum in the plane of chains of the same kind (along the axis c) in units of c^{-1} (c is the distance between chains along the axis c). To describe the motion of the electrons in the direction of the axis a we make use of the discrete coordinate m—the label of the unit cell, which contains two layers of acceptor and donor chains.
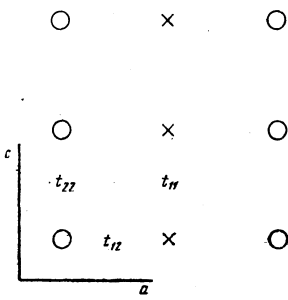
FIG. 1. Structure of the TTF-TCNQ crystal in the plane perpendicular to the chains; the TTF donor (D) chains are denoted by $\bigcirc$ and the TCNQ acceptor (A) chains by X; the transverse resonance integrals t_{11}, t_{22}, and t_{12} correspond to transitions between neighboring atoms of chains AA, DD, and AD, respectively.

The system of equations for the Green functions has the form

$$\langle G_{11}(m)\rangle = \langle G_{11}{}^0\rangle t_{12}[\langle G_{21}(m)\rangle + \langle G_{21}(m-1)\rangle] + \langle G_{11}{}^0\rangle \delta_{mn},$$

$$\langle G_{21}(m)\rangle = \langle G_{22}{}^0\rangle t_{12}[\langle G_{11}(m+1)\rangle + \langle G_{11}(m)\rangle],$$

(11)

where δ_{mn} is the Kronecker symbol. Going over to the momentum representation along the axis a and measuring the corresponding momentum p_y in units of the inverse spacing a^{-1} between the chains along the axis a, we obtain the following expressions for the Green functions:

$$\langle G_{11}(p_x, p_x, p_y)\rangle = \frac{\langle G_{11}{}^0\rangle}{1 - 2t_{12}{}^2\langle G_{11}{}^0\rangle\langle G_{22}{}^0\rangle(1 + \cos p_y)},$$

$$\langle G_{12}(p_x, p_x, p_y)\rangle = \frac{t_{12}(1 + e^{-ip_y})\langle G_{11}{}^0\rangle\langle G_{22}{}^0\rangle}{1 - 2t_{12}{}^2\langle G_{11}{}^0\rangle\langle G_{22}{}^0\rangle(1 + \cos p_y)} = \langle G_{21}(p_x, p_x, -p_y)\rangle.$$

(12)

In the calculation of $X_{\alpha\beta}{}^0$ we make use of the expressions (12) for the one-electron Green functions, in which we perform an expansion in the quantities $t = (t_{11}, t_{22}, t_{12})$; the expansion parameter is $t\tau \ll 1$ (we assume that $\varepsilon_F\tau \gg 1$; otherwise, the parameter of the expansion in t is the ratio $t/\varepsilon_F \ll 1$). The quantity $\operatorname{Im}\chi(n, \alpha, \omega_e)$ is determined by integrating $\operatorname{Re}X_{\alpha\alpha}(q, 0, \omega_e)$ over q. The principal contribution to this integral for T, ω_e, $\tau_\alpha{}^{-1} \ll \varepsilon_{F\alpha}$ is given by the regions of integration over q_x near the longitudinal-momentum values $q_x \approx 0$ and $q_x \approx 2k_{F\alpha}$, inasmuch as a small energy transfer is associated only with transitions of electrons near the Fermi surface. We shall consider first the expression for $X_{\alpha\alpha}(q, 0, \omega_e)$ in the region of small momenta q_x. Assuming that $\omega_e\tau_\alpha \ll 1$ and $q_x v_\alpha\tau_\alpha \ll 1$ we obtain

$$X_{11}(q, 0, \omega_e) = G_2[G_1G_2 - 64t_{12}{}^2[v_1v_2(v_1{}^{-1}\tau_1{}^{-1} + v_2{}^{-1}\tau_2{}^{-1})^2]^{-1}\cos^2(q_y/2)]^{-1}$$

$$G_1(q_x, q_x, \omega_e) = -i\omega_e + (q_xv_1)^2\tau_1 + 8t_{12}{}^2\left(\frac{1}{v_1\tau_1} + \frac{1}{v_2\tau_2}\right)^{-1}v_2{}^{-1}$$
$$+ 8t_{11}{}^2\tau_1\sin^2(q_x/2),$$

(13)

and G_2 is obtained from G_1 by the interchange of indices $1 \rightarrow 2$. From (13) it is clear that, with the condition we have used ($\omega_e\tau_\alpha \ll 1$), the propagation of spin excitations with small momenta q has a diffusive character. (The opposite case of coherent propagation of excitations with small momenta q is realized for $\omega_e\tau_\alpha \gg 1$). We note that at room temperatures in quasi-one-dimensional compounds the condition $\omega_e\tau_\alpha \ll 1$ is fulfilled by a large margin even in fields of the order of 100 kOe

($\tau_\alpha{}^{-1}$ reaches 3×10^{14} sec^{-1} at $T = 300$ K in TTF-TCNQ, and $\omega_e\tau \approx 10^{-3}$ for $H = 100$ kOe).

However, in TTF-TCNQ at room temperature the quantity $\varepsilon_F\tau_\alpha$ only attains values of $2 - 3$, so that the condition we have used ($\varepsilon_F\tau_\alpha \gg 1$) is fulfilled at the limit. The expression (13) makes it possible to find the coefficients of diffusion along the crystal axes b, c, and a, and then the corresponding expressions for the electrical conductivity along the axes b, c, and a:

$$\sigma_a = 4e^2 a t_{12}{}^2 \bigg/ \left(\frac{v_1}{\tau_2} + \frac{v_2}{\tau_1}\right)\pi\hbar^3 c,$$

$$\sigma_b = e^2(v_1\tau_1 + v_2\tau_2)/\pi\hbar ac,$$

$$\sigma_c = 4e^2 c\left(\frac{t_{11}{}^2\tau_1}{v_1} + \frac{t_{22}{}^2\tau_2}{v_2}\right)\bigg/\pi\hbar^3 a.$$

(14)

The expression (13) that we have obtained differs from the corresponding phenomenological expressions proposed in Refs. 1 and 3; moreover, it does not reduce to them even in the limit of small momenta q_x and q_y. We note also that the region of applicability of (13) is not bounded by small transverse momenta, and this is extremely important for the quantitative determination of the relaxation rate by means of (2) and (9), since in the integration over q_x and q_y all the regions of integration give a comparable contribution. We can now substitute (13) into (9) and perform the integration over the region of small momenta q_x. The integral over q_x with the function (13) converges at the upper limit, and the important contribution is given by momenta $q_x \lesssim (\omega_e/\tau)^{1/2}v^{-1} \ll \tau^{-1}v^{-1}$. This estimate justifies our restriction to just the first term of the expansion in vq_x, since the expansion parameter is the quantity $vq_x\tau$ (or vq_x/ε_F). Performing the integration over the momentum q_x we obtain the contribution to $\omega_e{}^{-1}\operatorname{Im}\chi(n, 1, \omega_e)$ from the diffusive propagation of the spin excitations, in the form

$$\omega_e{}^{-1}\operatorname{Im}\chi(n, 1, \omega_e) = \chi_0{}^0\frac{2\tau_1{}^{\frac12}}{\pi^2\tau_1}\left(\frac{v_2}{v_1}\right)^2\frac{b}{v_2}F_1(\omega_e),$$

(15)

where b is the distance between molecules along the axis b, and

$$F_1(\omega) = \int_0^{\pi/2} dx \int_0^{\pi/2} dy \left\{\frac{1}{2}\left(\frac{f_{1+}}{|f_1|} + \frac{f_{2+}}{|f_2|}\right) - \frac{(T_- \sin^2 x + g_-)A_1 + \omega WA_2}{A_1{}^2 + A_2{}^2}\right\}$$

(16)

here,

$$A_{1,2} = f_2'f_{1\pm} + f_1'f_{2\pm} \mp f_2''f_{1\mp} \mp f_1''f_{2\mp},$$

$$f_{1,2} = f_{1,2}' + if_{1,2}'' = -i\omega W_+ + T_+\sin^2 x + g_+ \pm (X_+ + iX_-),$$

$$f_{1,2} = [\tfrac12(|f_{1,2}| \pm f_{1,2}')]^{\frac12}, \quad X_\pm = [\tfrac12(|X| \pm X')]^{\frac12},$$

$$X = X' + iX'' = -\omega^2 W_- + (g_+{}^2 - g_-{}^2)\cos^2 y + (T_- \sin^2 x + g_-)^2$$
$$+ 2i\omega W_- (T_- \sin^2 x + g_-),$$

$$W_\pm = \tfrac12 \pm \tau_2 v_2{}^2/2\tau_1 v_1{}^2, \quad T_\pm = 4\tau_2(t_{11}{}^2 v_2{}^2 v_1{}^{-2} \pm t_{22}{}^2)/\hbar^2,$$

$$g_\pm = 4\tau_2 t_{12}{}^2(1 \pm \tau_2 v_2/\tau_1 v_1)/\hbar^2(\tau_2/\tau_1 + v_1/v_2).$$

We obtain the function $F_2(\omega)$ from (16) by interchanging the indices $1 \leftrightarrow 2$ in the expressions for $W_\pm$, $T_\pm$, and $g_\pm$; to obtain the expression for $\omega_e{}^{-1}\operatorname{Im}\chi(n, 2, \omega_e)$ it is necessary to make the same replacement in the expression (15). The dependence $F(\omega)$ is determined by the five parameters τ_1/τ_2, v_1/v_2, $t_{12}{}^2\tau_2$, $t_{11}{}^2/t_{12}{}^2$, and $t_{22}{}^2/t_{11}{}^2$. For

$$\omega_e \gg 8t_{12}{}^2(\tau_1{}^{-1} + \tau_2{}^{-1}v_1v_2{}^{-1})^{-1}/\hbar^2, \quad 8t_{11}{}^2\tau_1/\hbar^2 \text{ and } 8t_{22}{}^2\tau_2/\hbar^2$$

we obtain from (15) the "one-dimensional" regime $F(\omega_e) \sim \omega_e{}^{-1/2}$. As $\omega \to 0$ the function $F(\omega)$ tends to a

A. I. Buzdin and L. N. Bulaevskii   731

finite limit $F(0)$ because of the transverse motion of the electrons, and $F(0) \approx \omega_c^{-1/2}$, where $\omega_c = 8t^2\tau/\hbar^2$ for $t = t_{11} = t_{22} = t_{12}$ and $v_1 = v_2$, $\tau_1 = \tau_2 = \tau$.

We shall consider now the contribution to $\mathrm{Im}\chi(n, \alpha, \omega_e)$ from the integration over the region of momenta q_x near $2k_F$. Carrying out analogous calculations, we find that the contribution to the imaginary part of the susceptibility from momenta $q_x \sim 2k_F$ is small, in the parameter $\omega_e\tau \ll 1$, compared with the diffusive contribution that we have taken into account.

Up to now we have assumed the electrons to be non-interacting. It is not difficult, however, to take the Coulomb exchange interaction of the electrons into account in the framework of the random-phase approximation, in analogy with Ref. 8. Without dwelling on the calculations, we give the final result: in the expressions (15) for $\mathrm{Im}\chi(n, 1, \omega_e)$ it is necessary to make the replacements $t_{11}^2 \rightarrow \beta_1^2 t_{11}^2$, $t_{12}^2 \rightarrow \beta_1 t_{12}^2$, $v_1 \rightarrow \beta_1 v_1$, $\tau_1 \rightarrow \tau_1/\beta_1$, where $\beta_1 = 1 - V_{c1}/\pi v_1$; V_{c1} is the exchange Coulomb potential on the acceptor chain. The condition for applicability of the random-phase approximation is a weak Coulomb interaction, i.e., $1 - \beta_1 \ll 1$ and $1 - \beta_2 \ll 1$.

4. RELAXATION IN QUASI-ONE-DIMENSIONAL CRYSTALS WITH STRUCTURE OF THE HMTTF-TCNQ TYPE

In crystals of this type the donor and acceptor chains alternate along the two transverse directions of the axes **a** and **c** (see Fig. 2). The interaction of nearest molecules of neighboring chains is described by two transverse integrals t_1 and t_2.

We choose the x and y axes as shown in Fig. 2 and introduce discrete coordinates m and n among these axes. The indices 1 and 2 refer, as earlier, to the acceptor and donor chains. In the momentum representation (along x and y) we have equations for the Green functions $G_{\alpha\beta}(\mathbf{p})$:

$$G_{11}(\mathbf{p}) = G_{11}{}^0(p_z) + t_1 G_{11}{}^0(p_z)[1 + e^{-i(p_x+p_y)}]G_{21}(p_z) + G_{11}{}^0(p_z)t_2(e^{-ip_x} + e^{-ip_y})G_{21}(\mathbf{p}),$$

$$G_{21}(\mathbf{p}) = G_{22}{}^0(p_z)t_1[1 + e^{i(p_x+p_y)}]G_{11}(\mathbf{p}) + G_{22}{}^0(p_z)t_2(e^{ip_x} + e^{ip_y})G_{11}(\mathbf{p}). \tag{17}$$
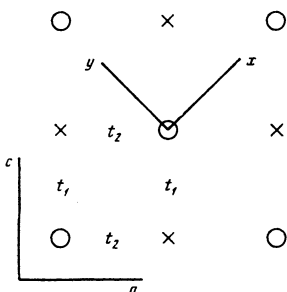
The solution of this system has the form

FIG. 2. Structure of the HMTTF-TCNQ crystal in the plane perpendicular to the chains; the donor chains are denoted by O and the acceptor chains by X; the transverse resonance integrals t_1 and t_2 correspond to transitions between neighboring donor and acceptor chains along the axes c and a, respectively; their difference is due to the anisotropy of the molecules.

$$G_{11}(\mathbf{p}) = G_{11}{}^0(p_z)[1 - 4G_{11}{}^0(p_z)G_{22}{}^0(p_z)[t_1\cos((p_x+p_y)/2) + t_2\cos((p_x-p_y)/2)]^2]^{-1},$$

$$G_{21}(\mathbf{p}) = [G_{22}{}^0(p_z)G_{11}{}^0(p_z)[t_1(1+e^{i(p_x+p_y)}) + t_2(e^{ip_x}+e^{ip_y})]] \times [1 - 4G_{11}{}^0(p_z)G_{22}{}^0(p_z)[t_1\cos((p_x+p_y)/2) + t_2\cos((p_x-p_y)/2)]^2]^{-1}. \tag{18}$$

Using the values of $G_{\alpha\beta}(\mathbf{p}, \omega)$ that we have found and expanding them in the parameter $t\tau$, we calculate the quantities $X_{\alpha\beta}{}^0$. For $\omega_e\tau \ll 1$ we obtain from (8) expressions for $X_{\alpha\alpha}(\mathbf{q}, 0, \omega_e)$ for small q_x:

$$X_{11}(\mathbf{q}, 0, \omega_e) = G_2(q_z, \omega_e)\left[G_1(q_z, \omega_e)G_1(q_z, \omega_e) \right.$$
$$\left. -64[v_1v_2(v_1^{-1}\tau_1^{-1} + v_2^{-1}\tau_1^{-1})^2]^{-1}\left[t_1^2\cos\left(\frac{p_x+p_y}{2}\right) + t_2^2\cos\left(\frac{p_x-p_y}{2}\right) \right]^2 \right]^{-1}$$

$$G_1(q_z, \omega) = -i\omega + (q_z v_1)^2\tau_1 + 8(t_1^2+t_2^2)v_2^{-1}(v_1^{-1}\tau_1^{-1} + v_2^{-1}\tau_1^{-1})^{-1},$$
$$G_2 = G_1(1 \leftrightarrow 2),$$
$$\sigma_a = 4e^2 t_1^2 a/\pi\hbar^3 c(v_1\tau_2^{-1} + v_2\tau_1^{-1}),$$
$$\sigma_c = 4e^2 t_2^2 c/\pi\hbar^3 a(v_1\tau_2^{-1} + v_2\tau_1^{-1}). \tag{19}$$

Integration over the longitudinal momentum q_z gives for the diffusive contribution to $\omega_e^{-1}\mathrm{Im}\chi(n, 1, \omega_e)$ the expression (15), where, in determining $F_1(\omega)$ from formula (16), it is necessary to put $T_\pm$ equal to zero and replace $t_{12}^2 \rightarrow t_1^2 + t_2^2$ and $\cos y \rightarrow [t_1^2\cos(x+y) + t_2^2\cos(x-y)]/(t_1^2+t_2^2)$. In the integration over q_z in the expression for $\mathrm{Im}\chi(n, \alpha, \omega_e)$ the region of momenta about $q_z = 2k_F$ gives the same small contribution as in the preceding section, and, consequently, may be disregarded in the determination of the dependence of the relaxation rate on the magnetic field.

At present there is very little experimental data on the dependence of the NMR relaxation rate on the magnetic field in compounds of the type HMTTF-TCNQ. We know of appropriate experimental results only for the compound HMTSF-TCNQ.[4] The data from measurement of the transverse conductivity in this compound[1] show that $\sigma_a/\sigma_c \gtrsim 10$.[4] Thus, the transverse anisotropy of the compound HMTSF-TCNQ is rather large $(t_1^2/t_2^2 \sim 10)$; the structural data also indicate this.

In crystals with $\hbar\tau^{-1} \gg t_1 \gg t_2$ we can distinguish a "one-dimensional" region, with the dependence $T_1^{-1} \sim H^{-1/2}$ in fields $\tau^{-1} \gg \omega_e \gg 8t_1^2\tau/\hbar^2$, and a "two-dimensional" region with the dependence $T_1^{-1} \sim \ln\omega_e$ in fields $8t_1^2\tau/\hbar^2 \gg \omega_e \gg 8t_2^2\tau/\hbar^2$. In the "two-dimensional" region the dependence $T_1^{-1}(H)$ for $\tau_1 = \tau_2 = \tau$ and $v_1 = v_2 = v$ has the form

$$T_1^{-1} = \frac{TA^2\hbar b}{\pi^2 g^2 \mu_B^2 v t_1\tau}\chi^0\ln\left(\frac{8t_1^2\tau}{\hbar^2\omega_e}\right) + C, \tag{20}$$

where the constant C describes the contribution that does not depend on the field. For $\omega_e \rightarrow 0$ we find for $T_1^{-1}(0)$ an expression that can be obtained from (20) by replacing ω_e by $8t_2^2\tau/\hbar^2$ and using a slightly different constant C (the difference in the constants C can be obtained by numerical calculations on the basis of the formulas (15), (16) with the replacement indicated above).

Experimentally the dependence $T_1^{-1}(H)$ in HMTSF-TCNQ has been investigated in fields from 10 to 100 kOe.[4] In this region, as can be seen from Fig. 3, the relaxation rate depends logarithmically on the field, in accordance with formula (20). The fact that the relaxation rate in HMTSF-TCNQ is not observed to ap-
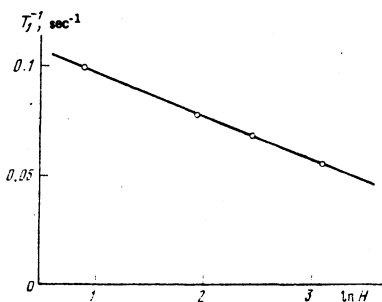
A. I. Buzdin and L. N. Bulaevskiĭ   732

FIG. 3. Dependence of the relaxation rate in the compound HMTSF-TCNQ on the magnetic field H (in kilo-oersteds); $\bigcirc$ are the experimental data of Ref. 4.

proach the "one-dimensional" dependence $T_1^{-1} \sim H^{-1/2}$ even in fields of the order of 100 kOe indicates the greater value (as compared with TTF-TCNQ) of the resonance integral t_1 (this conclusion is in agreement with the results of measurements of the anisotropy of the conductivity—in HMTSF-TCNQ the ratio $\sigma_b/\sigma_a \approx 33$, whereas $\sigma_b/\sigma_a = 120$ in TTF-TCNQ). The approach of T_1^{-1} to a constant with decrease of the field was not observed in Ref. 4, since measurements in weak fields were not made. We note that such measurements would give direct information on the quantity $t_2^2\tau$.

5. NMR RELAXATION IN LAYERED CRYSTALS

In layered crystals the ladder approximation is applicable under the same conditions as in a three-dimensional isotropic system, i.e., for $k_F l \gg 1$. In calculating the imaginary part of the local susceptibility we shall assume the motion in a layer to be isotropic, and describe transitions between layers in the tight-binding approximation, assuming that the resonance integral of the transition between layers $t \ll \tau^{-1}\hbar$, where τ is the mean scattering time of an electron in a layer. The calculations of the average of the product of one-electron Green functions are completely analogous to those described in Sec. 3, and the final result for $\chi(\mathbf{q}, \omega)$ for small momenta $q_{\parallel} = (q_x, q_y)$ within a layer $(q_{\parallel} v_F \tau \ll 1)$ has the form

$$\chi(\mathbf{q}, \omega) = \chi^0 \frac{8t^2\tau \sin^2(q_z/2) + \frac{1}{2}(q_{\parallel}v_F)^2\tau}{8t^2\tau \sin^2(q_z/2) + \frac{1}{2}(q_{\parallel}v_F)^2\tau - i\omega}, \tag{21}$$

where q_z is the momentum for motion of the electrons across the layers, in units of the inverse spacing between the layers. The imaginary part (the part of interest to us) of the local susceptibility is obtained by integrating $\omega_e^{-1}\mathrm{Im}\chi(\mathbf{q}, \omega_e)$ over $\mathbf{q}$. (The integration over large momenta $q_{\parallel}$ gives a contribution that is independent of ω for $\omega\tau \ll 1$). The dependence of the relaxation on the magnetic field is determined by the contribution to the integral over $q_{\parallel}$ from small momenta $q_{\parallel}$, i.e., by the integral of the expression (21) over $q_{\parallel}$ between 0 and $q_{\parallel} \approx 1/l$. As a result of the integration over $q_{\parallel}$ we obtain

$$T_1^{-1} = \frac{2A^2T\chi^0}{\sigma^2\mu_B^2v_F^2\tau}\int_0^{\pi/2}\ln[\omega_e^2\tau^2 + 64(\hbar^{-1}t\tau\sin q_z)^4]dq_z. \tag{21}$$

Thus, in strong magnetic fields $\omega_e \gg 8t^2\tau/\hbar^2$ (the "two-dimensional" regime), the relaxation rate in quasi-two-dimensional compounds increases logarithmically with

decrease of the magnetic field, but as $H \to 0$ the relaxation rate tends to a constant value because of the motion of electrons between layers. Thus, experiments on the observation of the dependence of the NMR relaxation rate on the magnetic field in layered crystals make it possible to determine the resonance integral t. However, the experimental observation of the logarithmic dependence is evidently possible in practice only in crystals with very weak electron tunneling between layers. In the intercalation layered crystals $TaS_2(aniline)_{3/4}$ and $TaS_2(Py)_{1/2}$, from data for the superconducting properties the quantity $8t^2\tau/\hbar$ corresponds to an energy of the order of 1-3 K (Ref. 10) and the logarithmic dependence of T_1^{-1} on H can be observed only in fields exceeding 30 kOe. In accordance with this, we can explain the result of Ref. 11: in the compound $TaS_2(Py)_{1/2}$ at room temperatures, no dependence of T_1^{-1} on the magnetic field was detected in fields up to 6 kOe.

6. DETERMINATION OF THE TRANSVERSE RESONANCE INTEGRALS FOR TTF-TCNQ

In Sec. 2 the expression (3) was obtained for the dependence of the relaxation rate on the magnetic field. It can be represented in the form

$$T_1^{-1}(H) = C_1^0 + C_{11}\frac{F_1(\omega_e)}{F_1(0)} + C_{12}\frac{F_2(\omega_e)}{F_2(0)}, \tag{23}$$

where $F_1(\omega_e)$ is determined by the expressions (16) and depends on the five parameters τ_1/τ_2, v_1/v_2, $t_{12}^2\tau_2$, t_{11}^2/t_{12}^2, and t_{22}^2/t_{12}^2. It is the last three parameters that characterize the transverse electron structure, and our problem is to determine them. The parameters C_α^0 and $C_{\alpha\beta}$ are determined by the interaction of the nuclear spins with the electron spins and by the character of the motion within the chains; the quantities C_{12} and C_{21} are determined entirely by the dipole-dipole interaction, while the parameters C_α^0 and $C_{\alpha\alpha}$ are determined also by the contact interaction.

For the determination of the unknown parameters we have at our disposal the dependence $T_{11}^{-1}(H)$ of the relaxation rate at the protons in $TTF(D_4)$-TCNQ samples (there are protons on the acceptor only—the donor molecule is deuterated) and the dependence $T_{12}^{-1}(H)$ of the relaxation rate at the protons in TTF-TCNQ(D_4) (Ref. 1). These experimental data are not sufficient to determine the numerous independent parameters of the problem. Since, in the experimental data, the error in the determination of the quantities $T_{1\alpha}^{-1}(H)$ is rather large, and the quantities $T_{1\alpha}^{-1}$ are not sensitive to all variations of the parameters, we shall make additional approximations in the expressions for T_1^{-1} and determine some of the parameters from other, independent measurements of the magnetic susceptibility and conductivity. First of all we put $C_{12} = C_{21} = 0$, since the quantities C_{12} and C_{21} are determined by the dipole-dipole interaction, which is small compared with the contact interaction. (By the estimates of Ref. 12, the parameters C_{12} and C_{21} amount to about 20% of the parameters C_{11}.) Furthermore, we shall not take into account the Coulomb repulsion of the electrons in the expressions for $F_1(\omega)$ and $F_2(\omega)$. We shall consider

the functions

$$\theta_a = \frac{T_{1a}^{-1}(H) - T_{1a}^{-1}(\infty)}{T_{1a}^{-1}(0) - T_{1a}^{-1}(\infty)} = \frac{F_a(\omega_e)}{F_a(0)}, \qquad (24)$$

which depend now on only five parameters. We shall determine the parameter v_1/v_2 from the data of Ref. 13, in which the ratio $\chi_1{}^0/\chi_2{}^0$ of the static susceptibilities of the acceptor and donor chains, equal in our approximation to v_2/v_1, was found. We take the parameter τ_1/τ_2 equal to v_2/v_1. This relation is valid if the electron mean free time is determined principally by the scattering of the electrons by intermolecular vibrations and the temperature is sufficiently high ($T \gg \omega_{Da}$, where ω_{Da} are the Debye frequencies of the chains). The three parameters associated with the transverse resonance integrals of interest to us remain unknown. In the situation when the parameters t_{11}, t_{12}, and t_{22} do not differ very much, the function $F(\omega)$ depends essentially on only one parameter with the dimensions of frequency, which determines the crossover from the dependence $F(\omega) \sim \omega^{-1/2}$ to the dependence $F(\omega) = \text{const}$ as the frequency is lowered. Therefore, from the data for T_{11}^{-1} and T_{12}^{-1}, only two parameters can be determined sufficiently unambiguously: the absolute parameter $t_{12}{}^2 \tau_2$ and one relative parameter. To determine the second relative parameter we have used the ratio of the conductivities

$$\frac{\sigma_c}{\sigma_a} = \left(\frac{c}{a}\right)^2 \left(\frac{t_{11}{}^2}{t_{12}{}^2} + \frac{t_{22}{}^2 \tau_2 v_1}{t_{12}{}^2 \tau_1 v_2}\right) \bigg/ \left(\frac{v_2}{v_1} + \frac{\tau_1}{\tau_2}\right) \qquad (25)$$

and expressed the parameter $t_{22}{}^2/t_{12}{}^2$ in terms of the parameter $t_{11}{}^2/t_{22}{}^2$. The remaining two parameters $t_{11}{}^2/t_{12}{}^2$ and $t_{12}{}^2\tau$ were calculated from the data of Ref. 1 for $\theta_{1,2}(H)$ in TTF(D$_4$)-TCNQ and TTF-TCNQ(D$_4$) crystals, using the parameters $H_{1,2}$ determining the behavior of $\theta_{1,2}(H)$ in high fields, when $\theta_{1,2}(H) = (H_{1,2}/H)^{1/2}$. The calculation gives $t_{22}{}^2/t_{12}{}^2 = 2$, $t_{11}{}^2/t_{22}{}^2 = 3.5$, and $t_{22}{}^2\tau_2 = 0.31 \times 10^{11}$ sec^{-1} for $T = 298$ K, $v_1/v_2 = 3/2$ (Ref. 13), and $\sigma_c/\sigma_a = 8$ (Ref. 14). Using the parameters found, we calculated the curves $\theta_{1,2}(H)$ numerically. These calculated curves, together with the experimental data of Ref. 1, are given in Fig. 4. As can be seen from Fig. 4, the agreement of the calculated curves with the experimental points is perfectly good.[3]

We can now estimate the values of the transverse resonance integrals, if the quantity τ_2 is known. By taking $\tau_1^{-1} + \tau_2^{-1} = 0.32 \times 10^{15}$ sec^{-1} from the optical measurements of Ref. 15, we obtain $t_{22} = 14$ K, $t_{12} = 10$ K, and $t_{11} = 26$ K. For comparison we give the results of a calculation of the transverse resonance integrals by the method of molecular orbitals: $t_{22} = 2.5$ K, $t_{12} = 13$ K, and $t_{11} = 17$ K.[16] We can also verify the consistency of our parameters by calculating the absolute values of the conductivity σ_c from (14) and comparing it with the results of measurements of σ_c. The calculation gives a quantity of about 4 ohm^{-1} cm^{-1}; experimentally, $\sigma_c = 4 - 6$ ohm^{-1} cm^{-1} (Ref. 14). The agreement of the theory with the experimental data is perfectly good, even though we made a rather crude approximation, assuming the interaction of the electrons to be unimportant, in the calculations of $\theta_\alpha(H)$. In fact, however, allowance for the not very strong Coulomb interaction reduces principally to a renormalization of the parameters
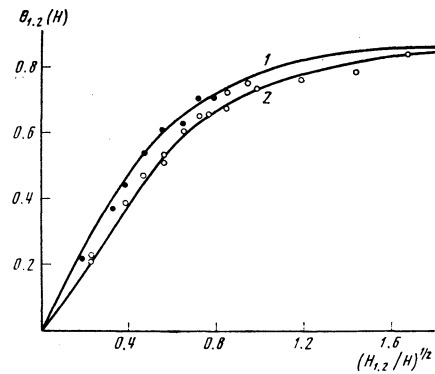

FIG. 4. Dependence of $\theta(H)_{1,2}$ on $(H_{1,2}/H)^{1/2}$ for TTF-TCNQ; ● and ○ denote the experimental data of Ref. 1, and the curves 1 and 2 are calculated theoretically for TTF(D$_4$) – TCNQ TTF-TCNQ(D$_4$), respectively.

used, and our calculations take into account that part of the interaction which reduces to a simple proportional renormalization of the quantities v_1, v_2, τ_1, and τ_2. Thus, the most important question becomes that of whether the repulsion of the electrons in TTF-TCNQ is large or small. Our model of weakly interacting electrons gives a good description of the experimental data for the NMR relaxation rate and conductivity and agrees with the results of quantum-chemical calculations[16] for the transverse resonance integrals. However, final conclusions on the role of the Coulomb repulsion in determining the relaxation rate and conductivity in TTF-TCNQ can be drawn only after consideration of these phenomena in the framework of a model with strong Coulomb repulsion.

We now discuss the question of what physical conclusions can be drawn from the results we have obtained for the transverse resonance integrals. The transverse resonance integrals in TTF-TCNQ are small compared with the characteristic parameters of the Peierls transition. Therefore, the gap that appears in the Peierls transition covers the entire Fermi "surface" in this compound and the transition in TTF-TCNQ leads to a dielectric ground state. In HMTSF-TCNQ the situation is different. In this compound the relaxation rate does not depend on the magnetic field in fields of up to 60 kOe (Ref. 4) and the width of the band in the direction of the axis a is found to be substantially greater than in TTF-TCNQ. Therefore, although a superstructure does appear in HMTSF-TCNQ, the corresponding gap only partially covers the Fermi surface and the compound HMTSF-TCNQ remains metallic at all temperatures.

The values of the transverse resonance integrals also make it possible to estimate the contribution of electron tunneling in the interaction of charge-density waves in TTF-TCNQ.[17] This contribution turns out to be unimportant in comparison with the contribution from the elastic interaction of displacements on different chains. This question is considered in more detail in Ref. 18.

A. I. Buzdin and L. N. Bulaevskiĭ   734

[1] The analogous dependence $T_1^{-1} \sim \omega_e^{-1/2}$ is also observed in dielectric crystals containing linear chains of localized electron spins.[5] In this case the quantity T_1^{-1} depends on the character of the propagation of the spin excitations in the one-dimensional chain of spins with Heisenberg interaction. For small frequencies ω_e the propagation of the excitations also turns out to be diffusive at sufficiently high temperatures (cf. Ref. 6).

[2] A contribution to the three-dimensional diffusion of the spin excitations is also given by the dipole-dipole interaction of the electrons. However, this contribution is two to three orders smaller than the contribution from tunneling of electrons between filaments, even in such strongly anisotropic crystals as TTF-TCNQ In dielectric crystals with spin chains the dipole-dipole interaction of the electron spins makes the principal contribution to the three-dimensional diffusion of the spin excitations of the electron system.

[3] In principle we could improve the procedure for determing the parameters t by using, e.g., the least-squares method in the entire range of variation of the magnetic field H. However, without an increase in the accuracy of the experimental measurement of T_1^{-1} this procedure will not give more-accurate values of t, since the experimental points coincide with our calculated curves within the experimental error bars. We note that the most important region for the determination of the parameters t is the region of low fields H, and up to now it is in precisely this region that the experimental errors for T_1^{-1} are rather large.

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Contribution to the theory of spatial dispersion and auxiliary light waves in the exciton absorption region

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The specific polarization of a crystal is expressed in terms of the total electric field in terms of the polarizability tensor $\kappa(\omega,k)$ or in terms of the external field with the aid of the tensor $\beta(\omega,k)$. It is shown that introduction of the dependence on k in β calls for knowledge of only the effective mass of the exciton, and when this dependence is directly introduced in κ the number of unknown additional parameters becomes much larger. The use of only the general scheme of quantum-mechanical calculation of β by supplementing it with macroelectrodynamic considerations has made it possible to determine $\beta(\omega,k)$ and to use the latter to determine $\kappa(\omega,k)$, the refractive indices of all the light waves, and their polarization in crystals with different symmetry. The dependences of the exciton energies and of the matrix elements of the dipole moment on $s\equiv k/|k|$ are determined in passim as $|k|\to0$. The connection between these quantities pertaining to different mutually degenerate excitons is obtained. These general results, deduced without using exciton models, cannot be obtained by direct quantum-mechanical calculation.

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1. TWO FORMS OF CRYSTAL POLARIZABILITY

The macroscopic specific dipole moment P of a crystal is traditionally expressed in terms of the macrofield E by the formula

$$P=\kappa E, \quad \kappa(\omega, k)=[\varepsilon(\omega, k)-1]/4\pi, \quad E, P\sim e^{i(kr-\omega t)}, \qquad (1)$$

where $\varepsilon(\omega,k)$ is the dielectric tensor of the crystal. The field E consists of the external field E_e and the field E' generated, without a time delay, by the electrons and