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1991 J. Phys.: Condens. Matter 3 429

(http://iopscience.iop.org/0953-8984/3/4/006)

J. Phys.: Condens. Matter 3 (1991) 429–436. Printed in the UK

The narrow band of electronic states localized at the interfaces of superlattices

V L Golo
Mathematics Department, Moscow University, Moscow 119899, USSR

Received 16 May 1990, in final form 28 September 1990

Abstract. Within the framework of tight-binding theory we have found a class of superlattices that possess a narrow band of electronic states localized at interfaces. We suggest that, if the electron–phonon interaction is small enough, it could preserve the existence of the narrow band and lead to a superconducting state formed by Cooper pairs of heavy electrons localized at interfaces.

1. Introduction

Electronic states seated at interfaces of a superlattice may have a band structure quite different from that of the bulk; for example, there may exist conductivity or even superconductivity related to interfaces. In this respect it is worth while to note that, as far as their crystalline structure is concerned, high-T_c oxide superconductors are layered materials, which may be viewed as a sort of superlattice, cooked in the natural process of preparing ceramics.

The fascinating idea that has been developing for some time is to grow high-T_c superconductors (perhaps of a nature different from that discovered by Bednorz and Müller (1986)) by employing the technique worked out for the manufacture of superlattices. In fact, Triscone *et al* (1989) prepared superlattices of the high-T_c superconductors $YBa_2Cu_3O_7$ and $DyBa_2Cu_3O_7$ with transition temperature T_{c0} above 85 K using the method of epitaxial growth. Considering the similarity between the crystalline structures of superlattices and high-T_c superconductors, in which the Cu–O planes form a kind of superlattice, we may expect that investigation of the properties of electronic states in superlattices in the normal state may have a bearing on the understanding of superconductivity (not necessarily of the cuprate type).

An important characteristic of the structure of electronic states is the bandwidth; in this paper we are going to show that in some simple cases very narrow bands of electronic states (i.e. very heavy electronic carriers) may localize at interfaces of superlattices, and result in a superconducting state due to the formation of Cooper pairs of heavy electrons.

Using the concept of narrow bands makes for understanding the phenomenon of high-T_c superconductivity. In this respect, it should be noted that the results of electrical transport measurements of YBaCuO and LaSrCuO oxides are difficult to explain if we confine ourselves to the picture of wide bands produced for these materials by calculations within the local-density approximation (LDA). In contrast, the concept of

0953-8984/91/040429 + 08 $03.50

narrow bands has turned out to be fruitful. Moshchalkov *et al* (1987) and Moschalkov (1988) came to the conclusion that high-T_c superconductors doped with strontium or oxygen should possess a narrow impurity band in the gap close to the valence band edge. Genossar *et al* (1989) suggested that the transport properties of these materials can be explained by the transport in a narrow band split off completely from the adjoining bands.

There are diverse opinions about the causes of narrow conduction bands in high-T_c materials. Matsumoto *et al* (1989) showed that the narrow band (of essentially two-dimensional origin due to the Cu–O planes) at the Fermi level of the oxide superconductors may be due to the mixing of the p and d electrons, allowing for a strong intra-atomic repulsion between d electrons. In contrast, Alexandrov *et al* (1986) showed that the narrow band of electronic states may appear due to some instabilities caused by strong electron–phonon interaction.

In this paper we study a novel mechanism for the formation of the narrow band of electronic states peculiar to the superlattice structure. We feel that it may have a bearing on superconducting materials, even though of a type different from those discovered by Bednorz and Müller (1986).

We consider a superlattice in which monatomic interfaces formed by a conductor separate slices of a large number of layers of a dielectric. Considering electronic states within the framework of the tight-binding model, we assume that the electronic atomic sites of interfaces and dielectric layers together form a simple cubic lattice and the amplitudes of electron transfer from a site in the dielectric to an adjacent site in either the dielectric or interface layers are equal to

$$\gamma = \gamma_{\text{diel-diel}} = \gamma_{\text{diel-interf}}. \tag{1}$$

Within interfaces the transfer amplitudes are generally different from that in the bulk,

$$\gamma_0 = \gamma_{\text{cond-cond}} \neq \gamma.$$

We consider only electronic transfers to nearest neighbours, and neglect intra-atomic repulsion between electrons. For the sake of simplicity, and taking into account that the model under consideration may be only a very crude picture of what happens in real life, we shall assume that the electrons are in the s state, neglect spin and suppose that $\gamma > 0$.

We shall show that a band generated by electronic states localized at interfaces of a superlattice may turn out to be narrow at the centre (or at the edge) of the Brillouin zone, if the transfer amplitudes satisfy a certain relation (see equation (11) in section 2). This narrow band lies above the bulk band, which is related to atomic layers confined between interfaces. If a sufficient number of electrons is provided, the Fermi level passes through the upper, narrow band generated by electronic states at interfaces, so that the interfaces form a 2D conductor, and the atomic layers between them (the bulk layers) a dielectric.

2. Electronic states localized at interfaces

To give a quantitative form to the picture of a superlattice we wish to study, let us write down its Hamiltonian, which comprises three terms,

$$H = H_i + H_b + H_{ib}$$

corresponding to interfaces (i), dielectric or bulk layers (b) and interaction terms

between them (ib), respectively. To simplify the notation let us choose such a spatial scale that the spacing of a lattice is equal to 1, so that the lattice sites are given by integer vectors

$$j = (j_1, j_2, j_3) \qquad j_1, j_2, j_3 = 0, \pm 1, \pm 2, \ldots .$$

In what follows we shall use the notations

$$\mathbf{1} = (1, 0, 0) \qquad \mathbf{2} = (0, 1, 0) \qquad \mathbf{3} = (0, 0, 1).$$

We shall assume that interfaces correspond to integer planes given by the equations

$$j_3 = kN \qquad k = 0, \pm 1, \pm 2, \ldots$$

with the number of layers between two adjacent interfaces equal to $N - 1$. Then the term H_i corresponding to interfaces reads

$$H_i = \sum_{j_1, j_2 = -\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \left(\alpha_0 c_j^+ c_j - \gamma_0 \sum_{i=1}^{2} (c_{j+i}^+ c_j + \text{HC}) \right)$$

with $j_3 = kN$. The term H_b reads

$$H_b = \sum_{j_1, j_2 = -\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \sum_{r=1}^{N-2} \left(\alpha c_j^+ c_j - \gamma \sum_{i=1}^{3} (c_{j+i}^+ c_j + \text{HC}) \right)$$

with $j_3 = kN + r$. The term H_{ib}, the interaction between interfaces and bulk layers, reads

$$H_{ib} = -\gamma \sum_{j_1, j_2 = -\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} [(c_{j'}^+ + c_{j''}^+) c_j + \text{HC}]$$

with $j_3 = kN$, $j_3' = kN + 1$ and $j_3'' = kN - 1$.

The Hamiltonian given above determines the dynamics of the one-particle problem. Since it contains only second-order terms, we can eliminate electronic operators related to sites inside the bulk (for example, with the help of functional integration, by employing the path integral for the description of Fermi fields (see appendix)) and obtain the equation for the spectrum of excitations localized at interfaces. The latter reads

$$E - \varepsilon_0(q) - 2\gamma^2 A(E, q) - 2\gamma^2 (\cos Q) B(E, q) = 0 \tag{2}$$

where $q = (q_1, q_2)$ is a 2D momentum in the plane of interfaces and Q is a momentum of excitations travelling over interfaces due to their interaction through bulk layers. The functions $A(E, q)$ and $B(E, q)$ are given by the equations

$$A(E, q) = \frac{2}{N} \sum_{r=1}^{N-1} \frac{\sin^2(\pi r/N)}{E - \varepsilon(q) + 2\gamma \cos(\pi r/N)}$$

$$B(E, q) = \frac{2}{N} \sum_{r=1}^{N-1} \frac{\sin(\pi r/N) \sin[\pi r(N-1)/N]}{E - \varepsilon(q) + 2\gamma \cos(\pi r/N)}$$

with $\varepsilon_0(q)$ and $\varepsilon(q)$ being the energies of excitations of momentum parallel to planes of interfaces

$$\varepsilon_0(q) = \alpha_0 - 2\gamma_0 \sum_{i=1}^{2} \cos q_i \qquad \varepsilon(q) = \alpha - 2\gamma \sum_{i=1}^{2} \cos q_i \qquad -\pi \leqslant q_1, q_2 \leqslant +\pi.$$

The RHS of the equation for $B(E, q)$ is an oscillating sum related to the interaction of interfaces through the bulk layers of the dielectric. Generally, we have no tools for studying it. But in the important situation when the number of layers between two adjacent interfaces is large, $N \gg 1$, there is the estimate

$$B(E, q) \sim 1/N$$

due to its oscillating nature. Consequently, for large N, i.e. thick slices of the dielectric between two adjacent interfaces, we may neglect the function $B(E, q)$ altogether, at least in a first approximation. Equally important, for large N we may change summation in the RHS of the equation for $A(E, q)$ for integration, and cast the function $A(E, q)$ in the integral form,

$$A(E, q) = \frac{1}{4\pi} \int_{-\pi}^{+\pi} dx \frac{\sin^2 x}{E - \varepsilon(q) + 2\gamma \cos x}. \tag{3}$$

It is easy to convince oneself that the following equations follow from equation (3):

$$2\gamma^2 A(E, q) = \begin{cases} E - \varepsilon(q) - \{[E - \varepsilon(q)]^2 - 4\gamma^2\}^{1/2} & E > \varepsilon(q) + 2\gamma \\ E - \varepsilon(q) + \{[E - \varepsilon(q)]^2 - 4\gamma^2\}^{1/2} & E < \varepsilon(q) - 2\gamma. \end{cases} \tag{4}$$

The first condition, $E > \varepsilon(q) + 2\gamma$, means that the energy of an excitation is above the bulk band (the band of excitations in the dielectric); the second, below the bulk band. The analytical continuation for the RHS in equation (4) gives the equation

$$2\gamma^2 A(E, q) = E - \varepsilon(q) - i\{[E - \varepsilon(q)]^2 - 4\gamma^2\}^{1/2} \tag{5}$$

for resonant states, i.e. lying inside the bulk band

$$\varepsilon(q) - 2\gamma < E < \varepsilon(q) + 2\gamma.$$

Using equations (4) and (5) and neglecting the function $B(E, q)$ we may cast equation (2) in the form

$$\varepsilon(q) - \varepsilon_0(q) = \kappa\{[E - \varepsilon(q)]^2 - 4\gamma^2\}^{1/2} \tag{6}$$

with $\kappa = -1, +1, i$ for excitations with energy above, below, inside the bulk band of dielectric layers.

For the upper band, $\kappa = -1$, the solution to equation (6) reads

$$E = \varepsilon(q) + \{[\varepsilon(q) - \varepsilon_0(q)]^2 + 4\gamma^2\}^{1/2}. \tag{7}$$

Since the sign at the radical in equation (6) is minus, we infer that the upper band is present for those values of momenta q for which we have

$$\varepsilon(q) < \varepsilon_0(q). \tag{8}$$

Let us consider constraint (8) to be true, and study equation (7) for small momenta, i.e. at the centre of the Brillouin zone. By expanding the RHS of (7) to first order in $q^2 = q_1^2 + q_2^2$ we get

$$E = \varepsilon(q = 0) + (\Delta^2 + 4\gamma^2)^{1/2} + q^2/2M \tag{9}$$

where

$$\Delta = \varepsilon(q = 0) - \varepsilon_0(q = 0) \qquad 1/2M = \gamma[1 + (1 - \gamma_0/\gamma)\Delta(\Delta^2 + 4\gamma^2)^{-1/2}].$$

From the equation given above we infer that the effective mass M tends to infinity as

$$(1 - \gamma_0/\gamma)\Delta(\Delta^2 + 4\gamma^2)^{-1/2} \simeq -1. \tag{10}$$

From (8) we infer $\Delta < 0$ and since $\gamma > 0$ we infer $\gamma_0 < \gamma$. In fact, it is not hard to see that

the stronger inequality $\gamma_0 < 0$ is to be satisfied. Equation (10) may be cast in the more explicit form

$$\alpha_0 \simeq \alpha + 4(\gamma_0 - \gamma) + 2\gamma^2[(\gamma - \gamma_0)^2 - \gamma^2]^{-1/2}. \tag{11}$$

Thus, we have come to the conclusion that electronic states localized at interfaces possess a very large effective mass if the parameters of tight-binding theory (α, α_0, γ, γ_0) are subject to constraint (11), in conjunction with $\gamma > 0$ and $\gamma_0 < 0$. The latter is unusual in tight-binding theory; the transfer integrals α and γ related to the matrix elements of the potential at a site and between adjacent sites are generally considered to be positive. In this respect, we would like to note that, in contrast to γ_0, the constant α_0 determined by equation (11) turns out to be positive for small negative γ_0, owing to the last term in equation (11); for example $\alpha_0 \simeq \alpha$ for $\gamma_0/\gamma \simeq -0.1$. The same analysis can be carried out for momenta $q_1, q_2 \simeq \pm\pi$, i.e. at the edge of the Brillouin zone.

The analysis of equation (6), similar to that given above, indicates that the lower band of states with energies below the bulk band is given by the equation

$$E = \varepsilon(\boldsymbol{q}) - \{[\varepsilon(\boldsymbol{q}) - \varepsilon_0(\boldsymbol{q})]^2 + 4\gamma^2\}^{-1/2}$$

in conjunction with the requirement $\varepsilon(\boldsymbol{q}) > \varepsilon_0(\boldsymbol{q})$, owing to the plus sign at the square root in equation (6). We see that, for a fixed momentum $\boldsymbol{q}$, states in the upper and lower bands generally cannot coexist simultaneously. The same is true concerning the resonant states.

It is worth noting that the influence of the interaction between interfaces accommodated through the function $B(E, \boldsymbol{q})$ is of order $1/N$, as was indicated earlier, so that it would give terms of order $1/N$ for a correction to solutions of the dispersive equations discussed above, and a splitting, also of order $1/N$, of energy bands. For instance, it would result in splitting the narrow band we have discussed above into a number of minibands, also narrow.

Concluding this section we wish to note that Dobrzynski and Mills (1973) found a splitting of electronic bands, above and below the bulk one, of electronic states localized at a (2×1) reconstructed (001) surface of a simple cubic lattice. They assume the transfer amplitudes be subject to a constraint that in our terms reads $\gamma \sim \gamma_0$. They do not consider narrow bands. Djafari-Rouhani *et al* (1985) studied electronic states localized at the surface of a superlattice consisting of thin alternating layers of two deposited compounds. We feel that their method can be used also for studying electronic states at interfaces of superlattices.

3. Conclusions

We have found that a narrow band of electronic states (large effective mass) may occur due to the topological structure of a body, i.e. the breaking of its crystalline symmetry by planes of interfaces of a superlattice. It is important that the use of the path integral involves no approximation (e.g. second-order expansion), gives the exact solution to the problem and brings about the main equation (2) describing the bands localized at interfaces without employing perturbation theory as regards the influence of the bulk band on the interface bands. For a large number, N, of bulk layers between two adjacent interfaces, and the analysis of equations (2)–(5) based on this assumption, the reciprocal effect of the interface bands on the bulk one is small (in contrast to the influence of the bulk on the interfaces, which increases with N). This statement can be proved along the

same lines as Ledermann's theorem, as is well known in the dynamical theory of lattices (see Maradudin *et al* 1963).

In this paper we have considered a one-particle problem: the electron–phonon interaction can also be allowed for, if it is small enough to be neglected in the first approximation, so that we may obtain the effect of the narrow band for suitable transfer amplitudes. Consequently, we have to require that the width W of the narrow band be larger than the correction given by the effective electron–phonon interaction V,

$$V \ll W. \tag{12}$$

Here it should be noted that the formation of heavy electrons within the framework of the model considered in this paper is different from the mechanism due to the strong electron–phonon interaction that results in the so-called small polarons due to lattice instabilities (see Alexandrov *et al* 1986, Zheng Hang 1989). Nonetheless, the superconducting state should take place in a situation similar to that of the small polarons, i.e. heavy electron carriers (the narrow band) and a weak effective electron–phonon interaction, subject to constraint (12).

As far as applications to existing materials are concerned, it should be noted that the LDA calculations of the band structure for high-T_c oxides (see Pickett 1989) do not show a narrow band similar to that obtained in the present paper. The reason for this may be twofold. Firstly, our model is perhaps too simplistic to be directly applied to high-T_c oxides; for example, we require that the number of bulk layers between two adjacent interfaces be large, whereas it is small for the oxides (to say nothing of our model's neglect of the effects of exchange and correlation, as the LDA also does). Secondly, the constraints on transfer amplitudes required by the narrow band may be incompatible with values of material constants used in the LDA calculations for the high-T_c oxides. Perhaps, our results should have a bearing on other materials.

In this respect it seems to be an interesting proposition that the superconductivity due to localized states studied in this paper could be similar to the quasi-2D superconductivity suggested for the first time by Ginzburg and Kirznitz (1964, 1967). In fact, if the number of atomic layers between two adjacent interfaces is large, the superlattices considered in this paper are sandwiches in the sense of Ginzburg and Kirznitz (1967), i.e. they accommodate the partitioning of the dielectric region and the conductor region. According to Ginzburg (1968, 1970) a superconducting state may settle on the conduction monolayer owing to an exchange by excitons, which propagate in the dielectric bulk region, between electrons at interfaces.

Appendix

We shall consider the path integral formulation of our problem at zero temperature. We need to write down the generating functional for the problem (see Popov 1976)

$$Z[\xi] = \int Dc^+ Dc \exp\left[\frac{\mathrm{i}}{\hbar}\int_{-\infty}^{+\infty} \mathrm{d}t \left(L + \sum_j (c_j^+ \xi_j + \xi_j^+ c_j)\right)\right]$$

with the Lagrangian

$$L = -H + \tfrac{1}{2}\sum_j (c_j^+ \cdot \mathrm{i}\hbar\partial_t c_j - \mathrm{i}\hbar\partial_t c_j^+ \cdot c_j).$$

Here c_j^+, c_j are Grassmann variables for fermionic fields, ξ_j^+, ξ_j are external sources, at

site $j = (j_1, j_2, j_3)$. The Green function for the system is derived from the generating functional (see Popov 1976). We need to find a transformation that splits up the interface and the bulk variables, and for that end we consider the translation

$$c_j^+ \to c_j^+ + \eta_j^+ \qquad c_j \to c_j + \eta_j$$

with η_j, η_j^+ being Grassmann functions at lattice sites; we assume that they are zero at interfaces. It should be noted that η_j^+ and η_j are Hermitian conjugate. Substituting them into the Lagrangian and requiring that terms linear in c_j

$$j = (j_1, j_2, j_3 = kN + 1) \qquad j = (j_1, j_2, kN - 1)$$

and their Hermitian conjugates be equal to zero, we obtain the equation for the fields η_j

$$i\hbar\partial_t \eta_j - \alpha\eta_j - \gamma \sum_{i=1}^{3} (\eta_{j+i} + \eta_j) = \gamma\delta_{l,1} c_{j_1 j_2 j_3 = kN} + \gamma\delta_{l,N-1} c_{j_1 j_2 j_3 = kN+N}$$

and similar equations for their Hermitian conjugates η_j^+. The Lagrangian itself takes the form

$$L = L_B^{\text{eff}} + L_0^{\text{eff}}$$

with L_B^{eff}, L_0^{eff} depending only on variables of bulk layers and interfaces, respectively. Thus we get the effective action for the system of interfaces

$$L_0^{\text{eff}} = \sum_{j_1, j_2 = -\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \left(\tfrac{1}{2}(c_j^+ \cdot i\hbar\partial_t c_j - i\hbar\partial_t c_j^+ \cdot c_j) - \alpha_0 c_j^+ c_j - \gamma_0 \sum_{i=1}^{2} (c_{j+i}^+ c_j + c_j^+ c_{j+i}^+) \right.$$
$$\left. - \tfrac{1}{2}\gamma(c_j^+ \eta_{j+\hat{3}} + c_{j+N\hat{3}}^+ \eta_{j+(N-1)\hat{3}} + \text{HC}) \right).$$

To get an explicit form for L_0^{eff} we may employ the Green function of the equation of motion for the fields η_j^+, η_j given above, with zero boundary conditions at interfaces. The Fourier transform of this function reads

$$G(E, j_1 - j_1^0, j_2 - j_2^0, kN + l, kN + l_0) = -\frac{2}{N(2\pi)^2} \int_{-\pi}^{+\pi} dq_1\, dq_2 \sum_{l=1}^{N-1}$$
$$\times \frac{\exp[-i\Sigma_{K=1}^{2} q_K(j_K - j_K^0)] \sin(\pi k l/N) \sin(\pi k l_0/N)}{E + \alpha + 2\gamma \Sigma_{i=1}^{3} \cos q_i + i \operatorname{sgn} E \cdot 0}$$
$$l, l_0 = 1, 2, \ldots, N - 1.$$

Thus we obtain the explicit form of the effective Lagrangian for surface fermionic fields (it is worth while to note that it is not local in time), which provides the equations of motion for the fields c_j^+, c_j, and after some computations we obtain the dispersive equation (2).

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