The possibility of bielectronic localisation due to the electron interaction with the anomalous soft mode

1989 J. Phys.: Condens. Matter 1 8859

(http://iopscience.iop.org/0953-8984/1/45/011)

J. Phys.: Condens. Matter **1** (1989) 8859–8864. Printed in the UK

The possibility of bielectronic localisation due to the electron interaction with the anomalous soft mode

A K Kazansky
Research Institute of Physics, Leningrad State University, Leningrad 198904, USSR

Received 5 December 1988, in final form 13 June 1989

Abstract. The enhancement of the electron–lattice interaction due to lattice anharmonicity is considered. When the lattice is anomalously soft the electron–lattice interaction generates a polaron state and bipolaron states of intermediate radius which are absent in the harmonic case. The Bose condensation of the bipolarons may give a mechanism of superconductivity.

The problem of the microscopic mechanism of high-T_c superconductivity is rather challenging. The principal question here concerns the relation between this phenomenon and the electron–lattice interaction. If this interaction plays a decisive role (there is some experimental evidence in favour of this assumption—see, e.g., Kim *et al* (1987), Herr *et al* (1987), Graves and Johnston (1988), Boolchand *et al* (1988), Yuen *et al* (1988), Xu *et al* (1988)), then one should consider another, then well established, Cooper's mechanism of electron pairing—this is shown unambiguously by a very small isotope effect. The new idea here is connected with the anharmonic character of these crystalline materials related to a mechanical instability. Phillips (1987a, b) argued that reconstruction and/or slow relaxation of the lattices take place in this case (an experimental study of the mechanical properties of the materials was reported by Shen Huimin *et al* (1987) and Bhattacharya *et al* (1988)), and that therefore the harmonic description of the lattice deformation fails. The calculations of Kress *et al* (1988) also show that the lattice of $YBa_2Cu_3O_7$ is close to instability. The possible role of anharmonicity of the lattice deformation in the mechanism of enhancement of the electron–lattice interaction was put forward by Zacher (1987), but he did not give any formulae. It is useful to mention here the experimental studies which show essential anharmonicity of the lattice vibration: Marsh *et al* (1988), Caponi *et al* (1987), Zhu Jingsheng *et al* (1988). The anharmonicity is included indirectly in the theory of Shi-jee Xiong (1988a, b), who considered the Jahn–Teller transition of oxygen atoms from position O(1) into position O(5) ($YBa_2Cu_3O_7$) as a mechanism of electron–lattice interaction. This approach resembles the theory of A15 superconductors proposed by Yu and Anderson (1984). Anharmonicity was also considered by Chaturverdi *et al* (1988), who put forward the Goldstone-type Hamiltonian which we also consider in this paper.

The key problem of the theory of anharmonic enhancement of the electron–lattice interaction is the search for the principal difference between the harmonic and anharmonic cases. This problem has not been discussed previously. We show here that in the anharmonic case there are singlet bipolaron states of intermediate radius whereas in the harmonic case even polaron states of this type are lacking. We stress that these bipolarons are essentially different from the well known negative-U centres proposed by Anderson (1975) for the harmonic case. It should be noted that the Anderson bipolarons and the Chakraverty bipolarons widely used in superconductivity theory (see, e.g., Alexandrov *et al* 1986, Alexandrov 1988, Chakraverty *et al* 1987, 1988, Wilson 1988) and the results obtained give hope of success. The transition from this type of polaron to ours was discussed in relation to the dependence on the space dimensionality by Emin and Holstein (1976) and Emin and Hillery (1988).

Let us consider the system of particles with coordinates x_i relative to the ith lattice cell. The energy of one electron interacting with the lattice is taken to be of the form

$$H^{(1)} = \sum_i \tfrac{1}{2}M\dot{x}_i^2 + \tfrac{1}{2}\tilde{a}_2 \sum_i x_i^2 + \tfrac{1}{4}\tilde{a}_4 \sum_i x_i^4 + \sigma \sum x_i n_i + \int (\hbar^2/2m)\,|\nabla\psi|^2\,\mathrm{d}^2r \qquad (1)$$

where $n_i = \int_{s_i} \mathrm{d}^2r\,|\psi|^2$ is the electron charge inside the ith cell (we suppose a two-dimensional character for the electron system). To simplify the study we consider the continuum variant of the Hamiltonian (1) and restrict ourselves to the stationary case:

$$H^{(1)} = \int [\tfrac{1}{2}M\dot{\varphi}^2 + \tfrac{1}{2}a_2\varphi^2 + \tfrac{1}{4}a_4\varphi^4 + \sigma\varphi n + (\hbar^2/2m)(\nabla\psi)^2]\,\mathrm{d}^2r \qquad (2)$$

where $a_2 = \tilde{a}_2/S$, $a_4 = \tilde{a}_4/S$, S is the area of the cell section ($S = ab$) and $\varphi(r)$ shows the lattice deformation.

The ground state of the system is determined by the minimum condition of the energy (2) relative to the variation of $\varphi(r)$ and $\psi(r)$ restricted to the normalisation condition

$$\int \psi^2\,\mathrm{d}^2r = 1. \qquad (3)$$

One finds the deformation $\varphi(r)$ in the ground state:

$$a^2\varphi + a_4\varphi^3 = \sigma|\psi|^2.$$

We compare here two cases: $a_2 = 0$ and $a_4 = 0$. In these cases we get the following functionals which should be minimised by the variation of ψ:

$$H^{(1)}_{(4)} = \int [(\hbar^2/2m)(\nabla\psi)^2 - \tfrac{3}{4}\sigma^{4/3}a_4^{-1/3}\psi^{8/3}]\,\mathrm{d}^2r \qquad (4)$$

and

$$H^{(1)}_{(2)} = \int [(\hbar^2/2m)(\nabla\psi)^2 - \tfrac{1}{2}(\sigma^2/a_2)\psi^4]\,\mathrm{d}^2x. \qquad (5)$$

Let us take any normalised function $\psi_1(x)$ and consider the set ψ_λ: $\psi_\lambda(x) = \lambda\psi_1(\lambda x)$. The functionals (4) and (5) take the following forms:

$$H^{(1)}_{(4)}(\lambda) = (\hbar^2/2m)\lambda^2 A_1 - \tfrac{3}{4}\sigma^{4/3}a_4^{-1/3}\lambda^{2/3}B_1 \qquad (6)$$

and

$$H^{(1)}_{(2)}(\lambda) = (\hbar^2/2m)\lambda^2 A_1 - \tfrac{1}{2}\sigma^2 a_2^{-1}\lambda^2 B_2. \qquad (7)$$

(The coefficients A_1, B_1, B_2 depend on the function ψ_1.) One may conclude that, in the case $a_2 = 0$, a value of λ exists for which $H^{(1)}_{(4)}$ is minimum—$\lambda = \sigma a_4^{-1/4}(mB_1/2\hbar^2 A_1)^{3/4}$—and the minimum value of $H^{(1)}_{(4)}$ is negative: $H^{(1)}_{(4)}(\mathrm{min}) =$

$-\frac{1}{2}\sigma_2 a_4^{-1/2} B_1(mB_1/2\hbar^2 A_1)^{1/2}$. In the case $a_4 = 0$ (equation (7)) one gets either $\lambda = 0$ (i.e., an unlocalised state) or $\lambda = \infty$ (i.e., a state localised on one site). We should mention here that in the one-dimensional case polaron states of intermediate radius exist even for the harmonic lattice (Davydov 1984, Heeger *et al* 1988). The dependence of the type of polarons on the space dimensionality was considered in detail by Emin and Holstein (1976) and Emin and Hillery (1988).

Let us now consider two electrons in the singlet state. For this state we may take the wavefunction ψ as a product of one-electron functions:

$$\psi(x_1, x_2) = \lambda^2 \psi_1(\lambda x_1)\psi_1(\lambda x_2). \tag{8}$$

In this case the energy function $H_{(4)}^{(\mathrm{II})}$ takes the following form:

$$H_{(4)}^{(\mathrm{II})}(\lambda) = 2[(\hbar^2/2m)\lambda^2 A_1 - \tfrac{3}{4}\sigma^{4/3} a_4^{-1/3} \lambda^{2/3} 2^{1/3} B_1]. \tag{9}$$

Minimising $H_{(4)}^{(\mathrm{II})}$ with respect to variation of λ, one finds that

$$H_{(4)}^{(\mathrm{II})}(\mathrm{min}) = 2^{3/2} H_{(4)}^{(\mathrm{I})}(\mathrm{min}). \tag{10}$$

Thus the bipolaronic state is favourable, and the energy gain is given by the expression

$$\Delta E = H_{(4)}^{(\mathrm{II})} - 2H_{(4)}^{(\mathrm{I})} = 2(2^{1/2} - 1)H_{(4)}^{(\mathrm{I})} \approx 0.8 H_{(4)}^{(\mathrm{I})}(\mathrm{min}). \tag{11}$$

We take the two simplest forms for ψ_1: $\psi_{1a} = (2/\pi)^{1/2}\exp(-r)$ and $\psi_{1b} = (2/\pi)^{1/2}\exp(-r^2)$. The values $H_{(4)a}^{(\mathrm{I})}$ and $H_{(4)b}^{(\mathrm{I})}$ are

$$\begin{aligned} H_{(4)a}^{(\mathrm{I})} &= -(\hbar^2/m)\lambda_a^2 = -(\hbar^2/m)^{-1/2}\sigma^2 a_4^{-1/2} 2^{1/2} \pi^{-1/2} (\tfrac{9}{32})^{3/2} \\ H_{(4)b}^{(\mathrm{I})} &= -2(\hbar^2/m)\lambda_b^2 = -2(\hbar^2/m)^{-1/2}\sigma^2 a_4^{-1/2} (2/\pi)^{1/2} (\tfrac{3}{16})^{3/2}. \end{aligned} \tag{12}$$

Thus the function ψ_{1b} is preferable ($H_b < H_a$).

It is of interest to express $H_{(4)b}^{(\mathrm{I})}$ in terms of the mean interelectron distance

$$\xi_b = \lambda_b^{-1}\left[\int \mathrm{d}^2 r_1\, \mathrm{d}^2 r_2 (r_1 - r_2)^2 \psi_1^2(r_1)\psi_1^2(r_2)\right]^{1/2} = \lambda_b^{-1}. \tag{13}$$

If we suppose that ξ is equal to the correlation length, we take its value as 16 Å ($YBa_2Cu_3O_7$, Abrikosov and Falkovsky 1988) and obtain

$$H_{(4)b}^{(\mathrm{I})} = -660(m_e/m)(k).$$

If we take for the effective electron mass the value $m = 6m_e$ (Gor'kov and Kopnin 1988), we get $\Delta E \sim kT_c$. One also may obtain an equation which restricts the possible values of the parameters of the model, σ and a_4:

$$\xi = (6m_e/m)^{3/4}\sigma^{-1} a_4^{1/4} (\hbar^2/m_e)^{3/4}. \tag{14}$$

What happens if a_2 is not equal to zero? The answer may be obtained only from a computer study and is as follows. For small a_2 (positive and negative) the picture is as described above. With the absolute value of a_2 increasing, the polaron state disappears first while the bipolaron state still exists (more comprehensive results will be published elsewhere). To illustrate these statements we consider here only the case of small positive a_2:

$$\delta H_{(4)}^{(\mathrm{I})} = a_2 \int \mathrm{d}^2 r \varphi^2(r) = a_2 \lambda^{-2/3} \int \mathrm{d}^2 r \psi_1^{4/3}(r)$$

$$\delta H_{(4)}^{(\mathrm{II})} = a_2 2^{2/3} \lambda^{-2/3} \int \mathrm{d}^2 r \psi_1^{4/3}(r).$$

One sees that $\delta H_{(4)}^{(\mathrm{I})}$ and $\delta H_{(4)}^{(\mathrm{II})}$ are both positive, but that $\delta H_{(4)}^{(\mathrm{II})} - 2\delta H_{(4)}^{(\mathrm{I})}$ is negative and with a_2 increasing the bipolaron state becomes more stable relative to decay into two polarons.

Considering a polaron and bipolaron moving uniformly, one may determine their effective masses. The corresponding contribution in the energy is equal to

$$\delta_v H = \tfrac{1}{2} v^2 \left[m + \frac{M}{S} \int \left(\frac{\partial \varphi}{\partial z} \right)^2 \mathrm{d}^2 r \right]$$

$$= \tfrac{1}{2} v^2 \left[m + \frac{M}{3S} \left(\frac{\sigma}{a_4} \right)^{2/3} (4\pi)^{1/3} \lambda^{4/3} \right].$$

If the velocity v is small enough, we may use the value of λ obtained above and obtain

$$\delta_v H = \tfrac{1}{2} v^2 \left(m + \frac{M}{S} \frac{\sigma^2}{a_4} \frac{m}{8\hbar^2} \right).$$

The effective mass of the polaron

$$M_{\mathrm{eff}} = m + \frac{M}{S} \frac{\sigma^2}{a_4} \frac{m}{8\hbar^2} \tag{15}$$

will be small enough ($M \sim 5m$) if $\sigma^2/a_4 \sim 6 \times 10^{-2}$ (here we use atomic units: $\hbar = m_e = e = 1$ and take $M = 32000$ ae, $S = 64$ ae). Equation (14) gives $\xi \sim 30 \sim \sigma^{-1} a_4^{1/4}$. Therefore one finds that $a_4 \sim 4 \times 10^{-4}$ au, $\sigma \sim 5 \times 10^{-3}$ au. These values of the parameters are reasonable enough, but we should stress that our estimate is rather approximate.

There are some other questions which we will consider only qualitatively here.

(i) The Coulomb repulsion should be taken into account. In its naive form the corresponding energy is

$$U_{\mathrm{C}} = \frac{1}{2\varepsilon_\infty} \int \mathrm{d}^2 r_1 \, \mathrm{d}^2 r_2 \frac{\psi^2(r_1 r_2)}{|r_1 - r_2|} \tag{16}$$

(ε_∞ is the dielectric constant), and in the formula (6) this gives an extra term $\varepsilon_\infty^{-1} \lambda B_3$. Thus, the bipolaronic state exists for any ε_∞, but if ε_∞ is not large enough this state becomes unstable relative to the decay into two polaron states. On the other hand, if we suppose that the screening length is rather small, the Coulomb interaction takes a contact form:

$$\tilde{U}_{\mathrm{C}} = \alpha \int \mathrm{d}^2 r \, \varphi^4(r)$$

which gives an extra contribution $\alpha B_4 \lambda^2$ in formula (6). One concludes that in this case the bipolaron state also exists and its stability condition is less restrictive than in the case (16).

(ii) We have considered here only singlet pairing. In the triplet state we cannot use the simplest representation (8) and the problem again needs a computer study. We have not found a triplet bipolaron state, but there is no exact proof of its absence.

(iii) We have not considered coupling of deformations in different cells, i.e. there is no gradient term in the Hamiltonian (2). This coupling gives an extra term proportional to $\lambda^{4/3}$ in formula (6), which is (for small λ) less than the binding energy proportional to $\lambda^{2/3}$. Thus, inclusion of this term complicates the picture and does not change the result qualitatively.

We have shown that the lattice anharmonicity may produce a drastic enhancement of the electron–lattice interaction. In this case polaron and bipolaron states are formed which are lacking in the harmonic lattice case. The Bose condensation of the bipolarons may provide a mechanism of superconductivity.

Acknowledgments

I am indebted to Professors K D Schotte and M Kulić for encouragement. The hospitality of Fachbereich Physik Freie Universität Berlin is also gratefully acknowledged.

References

Abrikosov A A and Falkovsky L A 1988 *Physica* C **156** 1–11
Alexandrov A S 1988 *Phys. Rev.* B **38** 925–7
Alexandrov A S, Ranninger J and Robaszkiewicz S 1986 *Phys. Rev. Lett.* **56** 949–52
Anderson P W 1975 *Phys. Rev. Lett.* **34** 953–5
Bhattacharya S, Higgins M J, Johnston D C, Jacobson A J, Stokes J P, Lavandowski J T and Goshorn D P 1988 *Phys. Rev.* B **37** 5901–4
Boolchand P, Enzweil R N, Zitkovsky I, Wells J, Bresser W, McDaniel D, Meng R L, Hor P H, Chu C W and Huang C Y 1988 *Phys. Rev.* B **37** 3766–69
Caponi J, Chaillout C, Hewat A W, Lejay P, Marezio M, Nguyen N, Raveau B, Soubeyronx T L, Tholence J L and Tournien R 1987 *Europhys. Lett.* **3** 1301–4
Chakraverty B K, Feinberg D, Hang Z and Avignon M 1987 *Solid State Commun.* **64** 1147–52
Chakraverty B K, Sarma D D and Rao C N R 1988 *Physica* C **156** 413–9
Chaturverdi S, Balakrishnan R, Sridhar R and Srinisaran V 1988 *J. Phys. C: Solid State Phys.* **21** L435–9
Davydov A S 1984 *Solitons in Molecular Systems* (in Russian) (Kiev: Naukowa Dumka)
Emin D and Hillery M S 1988 *Phys. Rev.* B **37** 4060–70
Emin D and Holstein T 1976 *Phys. Rev. Lett.* **36** 323–6
Gor'kov L P and Kopnin N B 1988 *Usp. Fiz. Nauk.* **156** 117–35
Graves P R and Johnston C 1988 *Solid State Commun.* **67** 113–8
Heeger A J, Kivelson S, Schrieffer J R and Su W-P 1988 *Rev. Mod. Phys.* **60** 781–850
Herr S L, Kamaras K, Porter C D, Doss M G, Tanner D B, Bonn D A, Greedan J E, Stager C V and Timusk T 1987 *Phys. Rev.* B **36** 733–5
Kim Y H, Heeger A J, Acedo L, Stucky G and Wudl F 1987 *Phys. Rev.* B **36** 7252–5
Kress W, Schröder U, Prade J, Kulkarni A D and de Wette F W 1988 *Phys. Rev.* B **38** 2906–9
Marsh B, Siegrist T, Fleming R M, Schneemeyer L F and Waszczak J V 1988 *Phys. Rev.* B **38** 874–7
Phillips J C 1987a *Phys. Rev. Lett.* **59** 1856–9
—— 1987b *Phys. Rev.* B **36** 861–3
Shen Huimin, Wang Yening, Zhang Zhifang, Zhang Shiyuan and Sun Linhai 1987 *J. Phys. C: Solid State Phys.* **20** L889–92
Shi-jee Xiong 1988a *J. Phys. C: Solid State Phys.* **21** L459–62
—— 1988b *J. Phys. C: Solid State Phys.* **21** 2899–909
Wilson J A 1988 *J. Phys. C: Solid State Phys.* **21** 2067–112

Xu M-F, Baum H-P, Schenstrom A, Sarma B K, Levy M, Sun K J, Toth L E, Wolf S A and Gubser D U 1988 *Phys. Rev.* B **37** 3675–8

Yu C C and Anderson P W 1984 *Phys. Rev.* B **29** 6165–86

Yuen T, Lin C L, Crow J E, Myer G N, Salomon R E, Schlottmann P, Bykowetz N and Herman W N 1988 *Phys. Rev.* B **37** 3770–3

Zacher R A 1987 *Phys. Rev.* B **36** 7115–7

Zhu Jingsheng, Song Jianxian, Wang Jun, Yang Zhougjin, Zhang Yuheng and Lung C W 1988 *J. Phys. C: Solid State Phys.* **21** L281–9