EFFECT OF LOW SYMMETRY ON ELECTRON-PHONON COUPLING IN PEROVSKITE SUPERCONDUCTORS

I.I. Mazin and S.N. Rashkeev

P.N. Lebedev Physical Institute, Academy of Sciences of the USSR, Leninsky Prospect, 53, 117924, Moscow, USSR

The electron–phonon coupling for La_2CuO_4-type superconductors is calculated in frameworks of rigid-muffin-tin approximation by two way: first, in spherical approximation of Gaspari–Gyorffy and, second, taking into account the proper local symmetry. In the second case electron–phonon coupling is a few times stronger than in the first one. We conclude that low local symmetry, especially on O_1 sites is to a great extent responsible for the strong electron–phonon coupling in perovskite compounds.

IT IS well-known that perovskite-like crystals usually have strong electron–phonon (EP) interaction. It is due to this fact that these compounds were chosen by Bednorz and Müller [1] as candidates to high-T_c superconductors. Surely there are several reasons why the EP coupling is strong in perovskites, in particular the strong ion potentials (ionic bonding) and/or some features of electronic structure. In some cases soft phonons may play an important part. It is interesting that there is another effect which is due to the low local symmetry around anions (e.g. O^{2-}) and which may enhance the EP coupling considerably.

The quantitative measure of the EP interaction is the EP coupling constant λ. Let us write it down after McMillan [2] as a ratio of the electronic contribution η and the average force constant $M < \omega^2 >$

$$\lambda = \sum_t \frac{\eta_t}{M_t < \omega_t^2 >}, \tag{1}$$

where M_t is the mass of an ion of kind t and $< \omega_t^2 >$ is its average phonon frequency. The electronic factor η is defined by the electronic structure and the crystal potential:

$$\eta_t = \frac{2n_t}{N(E_F)} \sum_{\substack{LL' \\ L_1 L_2}} N_{LL'}^t(E_F) V_{L'L_1}^t N_{L_1 L_2}^t(E_F) V_{L_2 L}^t, \tag{2}$$

where $N(E_F)$ is the density-of-states at the Fermi level, $L = (\ell, m)$, $N_{LL'}^t$ is the density matrix at the Fermi level in angular momenta representation and $V_{LL'}^t$ is the matrix element of the electron–ion interaction, n_t is a number of ions of kind t. Namely, when the wave function of an electron in the band λ with the wave vector k inside the particular atomic sphere t is written as

$$\psi_{k\lambda}(r) = \sum_{L,t} A_{Lt}^{k\lambda} \varphi_{\ell t}(|\mathbf{r}|) Y_L(\hat{\mathbf{r}}), \tag{3}$$

then $N_{LL'}^t$ is defined as

$$N_{LL'}^t = \sum_{k\lambda} (A_{Lt}^{k\lambda})^* A_{L't}^{k\lambda} \delta(E_F - E_{k\lambda}), \tag{4}$$

and

$$V_{LL'}^t = \int \varphi_{\ell t}(|\mathbf{r}|) Y_L^*(\hat{\mathbf{r}}) \, \delta V_T / \delta \mathbf{R}_t \, \varphi_{\ell' t}(|\mathbf{r}|) Y_{L'}(\hat{\mathbf{r}}) d\mathbf{r}, \tag{5}$$

where δV_t represents the change of the crystal potential after the displacement of the t-th ion by $\delta \mathbf{R}_t$. A popular approximation to $\delta V / \delta \mathbf{R}_t$ is the so-called rigid muffin-tin approximation [3]. In this approximation it is supposed that each ion potential move rigidly with the correspondent nucleus. The ion potential is usually assumed spherically symmetric (MT-potential). Then

$$\delta V(|\mathbf{r} - \mathbf{R}_t|)\delta \mathbf{R}_t = V'(|\mathbf{r} - \mathbf{R}_t|) \cdot (\mathbf{r} - \mathbf{R}_t)/|\mathbf{r} - \mathbf{R}_t|. \tag{6}$$

If one assumes local spherical symmetry for ion t then all non-diagonal components of $N_{LL'}^t$ vanish and equation (2) reduces to a simple formula [3]:

$$\eta_t = \frac{2n_t}{N(E_F)} \sum_{\ell} (\ell + 1) N_\ell^t(E_F) N_{\ell+1}^t(E_F)(W_\ell^t)^2, \tag{7}$$

where N_ℓ^t is the partial density-of-states

$$N_\ell^t(E_F) = \frac{1}{(2\ell + 1)} \sum_{k\lambda} \sum_m \left| A_{\ell m, t}^{k\lambda} \right|^2 \delta(E_{k\lambda} - E_F), \tag{8}$$

and

$$W_\ell^t = \int_0^{s_t} \varphi_{\ell t}(r) \varphi_{\ell+1,t}(r) V_t(r) r^2 dr. \tag{9}$$

Table 1. *Contributions of different ions to the Hopfield factor of tetragonal La_2CuO_4 calculated by Gaspari–Gyorffy formula (7) and with account of local symmetry (2) (in Ry/a_B^2). For explanation of η_t^I and η_t^{II} see footnote**

Ion	Hopfield factor from equation (2)			η (equation (7))
	η	η_{I}	η_{II}	
La	$4.148 \cdot 10^{-4}$	$2.532 \cdot 10^{-3}$	$-2.118 \cdot 10^{-3}$	$1.052 \cdot 10^{-3}$
Cu	$5.067 \cdot 10^{-2}$	$3.926 \cdot 10^{-2}$	$1.141 \cdot 10^{-2}$	$1.846 \cdot 10^{-2}$
O_I	0.244	0.236	$8.231 \cdot 10^{-3}$	$6.570 \cdot 10^{-2}$
O_{II}	$3.492 \cdot 10^{-3}$	$6.862 \cdot 10^{-3}$	$-3.370 \cdot 10^{-3}$	$1.846 \cdot 10^{-3}$

Equation (6) is known as the Gaspari–Gyorffy formula has proven to be very useful for quantitative calculation of the EP coupling in classical superconductors: transition metals, carbides, nitrides etc. It is not surprising because in these crystals all ions has local environment of cubic symmetry which is high enough. It was shown [4, 5] that for cubic symmetry equation (7) is strictly valid when $\ell \leqslant 2$ are taken into account and only a small correction appears for $\ell = 3$.

The same approach has been recently used for high-T_c oxides: $La_{2-x}Sr_xCuO_4$ [6, 7] and $YBa_2Cu_3O_7$ [8]. For the first one the EP coupling was found to be not small but in order to get desired values of λ $(1 \div 2)$ one had to assume comparatively soft phonons (of the order of 300 K for oxygen). For the 1-2-3 compound the obtained values of η were of the same order that in $La_{2-x}Sr_xCuO_4$ and hence obviously insufficient.

However, in perovskites (even in cubic ones) the local environment of the oxygen atoms has very low symmetry so the validity of the equation (7) is quite doubtful. In order to find the effect of this low symmetry we have performed calculations of η for $La_{2-x}Sr_x CuO_4$ by use of the equation (7) as well as of the

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* In fact we made use of equation (6) to reduce equation (2) to more convenient form

$$\eta_t = \frac{8\pi}{3} \frac{n_t}{N(E_F)} \sum_{\ell \ell'} W_{\ell}^t W_{\ell'}^t \sum_{\substack{mm' \\ \mu}} \left[N_{LL'}^t g_{\Lambda',1\mu}^{L'} N_{\Lambda'\Lambda}^t g_{\Lambda,1\mu}^{L} + (-1)^\mu N_{\Lambda L'}^t g_{\Lambda',1\mu}^{L'} N_{\Lambda'\tilde{L}}^t g_{\tilde{\Lambda},1(-\mu)}^{\tilde{L}} \right] = \eta_t^I + \eta_t^{II}$$

where $\Lambda' = (\ell' + 1, m' - \mu)$, $\Lambda = (\ell + 1, m - \mu)$, $\tilde{\Lambda} = (\ell + 1, m + \mu)$, $g_{LL'}^{L''}$ is Gaunt coefficient. The first term here in case of spherical symmetry reduces to the usual Gaspari–Gyorffy formula (7) and the second one vanishes identically.

equation (2) (Table 1). We have found that EP coupling due to O_I atoms increased by a factor of 3.7. Even for Cu atoms which has higher local symmetry but also lower than cubic η increased by 170%. The same effect should be even more prominent in $YBa_2Cu_3O_7$.

What does this result mean from the physical point of view? One may interpret it as follows: Let us suppose that there is a hypothetical material which includes Cu and O and has the same electronic structure, as $La_{2-x}Sr_xCuO_4$ the same ion potential and the same phonons but with atoms of both kinds having cubic local symmetry (for instance, CsCl of NaCl lattice). What would be the difference between λ in this compound and λ in the perovskite-like superconductor? We can answer this question at least in case of La_2CuO_4-type compounds. The answer is that λ would be a few times smaller. In other words, one of the reasons of strong EP interaction in $La_{2-x}Sr_xCuO_4$ is due to its low local symmetry. We believe that the same is true for other high T_c superconductors.

It is important that it is the *local* symmetry and not the whole lattice symmetry which is crucial. We may demonstrate it by an example of HCP yttrium. Y crystallize in HCP lattice with $c/a = 1.57$ close to ideal $c/a = 1.66$. The lattice symmetry is hexagonal and then far from cubic. However, the nearest environment of each atom is quite symmetric (nearly the same as in FCC lattice). As a result we have found that equation (6) works quite well in this case (Table 2). Therefore the large effect in perovskite is due just to the local symmetry.

Another conclusion of this work is that at least in $La_{2-x}Sr_xCuO_4$ even such reasonable values of the average phonon frequency as 300–400 K may provide high EP coupling ($\lambda \sim 2 \div 3$). One should however keep in mind that the rigid-MT approximation itself requires verification for such compounds.

We hope that this paper will stimulate band theorists to calculate (or to recalculate) the rigid-MT λ for other high-T_c superconductors.

Table 2. Calculated Hopfield factor for HCP-yttrium (in Ry/a_B^2). For equation (2) we give also the contributions to η^I and η^{II} terms from different ℓ and ℓ' in equation (2') and from different ℓ in equation (7)

η (equation (2))				η (equation (7))	
$3.131 \cdot 10^{-2}$				$3.063 \cdot 10^{-2}$	
ℓ	ℓ'	η_I	η_{II}	ℓ	η
0	0	$1.263 \cdot 10^{-3}$	$< 10^{-5}$	0	$1.097 \cdot 10^{-3}$
0	1	$< 10^{-5}$	$1.021 \cdot 10^{-3}$		
0	2	$-6.784 \cdot 10^{-4}$	$< 10^{-5}$		
1	1	$1.941 \cdot 10^{-2}$	$< 10^{-5}$	1	$1.994 \cdot 10^{-2}$
1	2	$< 10^{-5}$	$-6.410 \cdot 10^{-4}$		
2	2	$1.092 \cdot 10^{-2}$	$< 10^{-5}$	2	$1.005 \cdot 10^{-2}$

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