Eliashberg theory and high-T_c superconductivity

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Abstract. The superconducting transition temperatures in the new perovskites are calling for an explanation. In this paper we would like to show how it is possible to extract, from Eliashberg theory of superconductivity, enough information to gain an important insight into the system from which some answers can be obtained. We illustrate our ideas with the example of the Nb–Ge system for which the necessary experimental information is available. This analysis can be carried out in part on new superconducting perovskites with $T_c = 40$ K, where the electron-phonon interaction seems not to be so easily disregarded, at least as part of the interaction.

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The main result of Eliashberg theory of superconductivity are the gap equations [1]. From the linearized version, valid at T_c one can extract information about important thermodynamic parameters as the Coulomb repulsion parameter, μ^*, which can be fitted to the experimental T_c [2]. Another useful information is the functional derivative [3], $\delta T_c/\delta\alpha^2 F(\omega)$, from which one can evaluate the effectiveness of the phonons at different frequencies in building up the superconducting state. In particular, one can show that the phonons at $\omega \sim 7KT_c$ are the most effective.

The nonlinearized version of the Eliashberg gap equation is the basis on which one can calculate the free energy difference through the known formula by Wada [4]. The thermodynamic functions are calculated using the usual formulae from statistical mechanics [5]. An analytic continuation of the gap function as it is obtained from the solution of the non-linearized version of the gap equations to the real frequency axis, gives the gap edge, Δ_o, the fundamental BCS [5] parameter that can be measured directly from tunnelling experiments or infrared spectroscopy.

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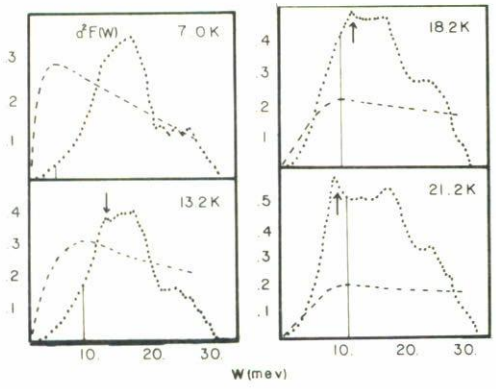

FIGURE 1. Evolution of the Nb–Ge system towards stochiometry. The dotted curve is the Eliashberg function, $\alpha^2F(\omega)$, and the dashed curve is the functional derivative of T_c with $\alpha^2F(\omega), \delta T_c/\delta\alpha^2F(\omega)$. Each Ge concentration is labelled with the corresponding T_c: 16.7% (7.0 K), 21.3% (13.2 K), 22.3% (18.2 K), 25.7% (21.2 K). The arrows indicate the evolution of the peak due to the formation of the chains characteristic of the A–15 structure. Notice how this peak goes through the maximum of the functional derivative, indicating that the highest T_c will be around stochiometry and that the process is optimized, a well known fact, (see text). The units for the intensity are arbitrary.

In Fig. 1, we show an example of the use of Eliashberg theory to analyse the origin of high T_c in the most important superconductivity system until 1985: Nb_3Ge [6,7]. Different samples with different concentration of Ge prepared by Kihlstrom and Geballe [8], and tunnelling experiments were performed from which the Eliashberg functions and the Coulomb repulsion parameters, μ^*, were obtained by inversion of the I–V characteristics using the program that takes into account the proximity effect [9].

Fig. 1 is a picture of what happens while Nb_3Ge goes to the configuration in which it has the highest T_c. We show here two curves for each system. The dotted curve is the Eliashberg function, $\alpha^2F(\omega)$, and the dashed curve is the functional derivative of T_c with $\alpha^2F(\omega), \delta T_c/\delta\alpha^2F(\omega)$. Each is labelled with the corresponding T_c. We emphasize that the samples differ in composition (Fig. 1). The crystal structure of all of them is the A–15, but since there is not enough Ge atoms in the low temperature samples we expect the actual crystal structure to be a slight deformation of the A–15. We do not expect that another structure occurs since the difference in composition is not pushed as far as that. X-rays characterization confirms this picture.

As we stated above, the Eliashberg functions, $\alpha^2F(\omega)$, presented here are all experimental curves. The functional derivatives of the critical temperature, T_c, with $\alpha^2F(\omega)$, $\delta T_c/\delta\alpha^2F(\omega)$, where obtained from the numerical solution of Eliashberg gap equations at T_c. The data that we used for this purpose are the just mentioned experimental Eliashberg functions and the *measured* T_c. The Coulomb repulsion

parameter, μ^*, was fit so that we get consistency between the experimental data and Eliashberg theory. This procedure takes care of the very big uncertainty with which μ^* is determined from experiment [3].

It is very important, for this analysis, to understand the physical meaning of $\delta T_c/\delta\alpha^2F(\omega)$. This function, by definition, gives the change in T_c due to any change in the Eliashberg function. Consequently,

$$\Delta T_c = \int_0^\infty \frac{\delta T_c}{\delta\alpha^2F(\omega)}\Delta\alpha^2F(\omega)d\omega. \tag{1}$$

As we can see from Fig. 1, $\delta T_c/\delta\alpha^2F(\omega)$ is always positive. Then, Eq. (1) is telling us that ΔT_c will be positive if $\Delta\alpha^2F(\omega)$ is so, $\Delta\alpha^2F(\omega)$ will be positive whenever we add some weight to $\alpha^2F(\omega)$. It will be negative in the opposite case. We can add or take weight to or from the Eliashberg function in several ways.

In this example, the way to add it was the approach to stochiometry. We can see that the system actually goes to higher temperatures. The preparation of the sample started with 17% Ge content and ended with 25.7%. Stochiometry is obviously 25% and so it was overpassed in Ge content during this experiments.

To understand better the physical meaning of $\delta T_c/\delta\alpha^2F(\omega)$, let us imagine that we can add a delta function to $\alpha^2F(\omega)$ at the frequency we want. Where should we add it to get a higher enhancement in T_c? Since the functional derivative is always positive, we know that we will enhance T_c anyway. But since the functional derivative goes through a maximum, it is in this frequency where it will do best, that is, where it will give the highest enhancement in T_c. It is possible to show that the existence of this maximum is related to the importance of relaxation effects in the electron phonon interaction as it enters superconductivity. As we can see from Fig. 1, this curve has a sharper maximum for the sample with the lowest T_c. This maximum gets broader as T_c goes up. In general, we can say that the maximum is sharp for weak coupling and it gets broader as the coupling strengthens. It is also possible to show that the maximum is located around $7KT_c$ for any superconductor (K is the Boltzman constant). So the answer to our question is that the highest enhancement in T_c will be obtained if we put our delta function at $\omega = 7KT_c$.

To use this information the next step is to understand what can be and what cannot be realizable within our system. According to what we said before, the best thing to do is to pile up all the weight of $\alpha^2F(\omega)$ at $\omega = 7KT_c$. So this is the goal. This will give the highest possible T_c this material can give. But only the deep knowledge of the system will tell us how far we can actually follow this process (see below). Also, once this is achieved there is nothing else to do. For a higher T_c we have to go to another system.

An example of what can be done in practice is Fig. 1. The system Nb–Ge was changed in composition in order to find the one that would give the highest T_c. We will show in what follows that this process amounts to add weight to the Eliashberg function at almost all the frequencies with particular emphasis in the frequency where the maximum in the $\delta T_c/\delta\alpha^2F(\omega)$ is ($\omega = 7\ K\ T_c$). We will also conclude that the process in this particular system is optimized and that therefore it was

not expected that a higher T_c could be obtained in the Nb–Ge system, a very well known fact confirmed by almost 15 years of experimental research.

In Fig. 1, we have presented four different compositions of the Nb–Ge system. As we stated before, we have drawn the Eliashberg function and the functional derivative for each of them.

Let us examine system by system. We start with the system with $T_c = 7$ K. Let us find the maximum of the functional derivative for this system and look how high the intensity of the Eliashberg function is there (Fig. 1). At this frequency the coupling between phonons and electrons is best for superconductivity. But we see that there is very little weight in the corresponding Eliashberg function of this system, and consequently T_c is the lowest. Let us now compare to the situation in the system with the next higher T_c (13.2 K). There is more weight in $\alpha^2 F(\omega)$ below the optimal frequency. There is also more weight everywhere (the scale is not the same). Notice that at this frequency a peak begins to form and that it is the nearest peak to the optimal position for this composition. so this is the peak (see the arrow in Fig. 1) that is playing the most important role in increasing T_c. Compared to the system with $T_c = 7$ K, composition goes towards stochiometry.

The next system shows that getting closer to stochiometry improves the situation even more. We get an overall enhancement of the Eliashberg function with particular emphasis to the optimal position. And we get, consequently, a higher T_c. It is to be noticed that the new peak that began to appear already in the system with $T_c = 13.2$ K is now a very sharp peak that grows in intensity and moves to the optimum frequency from composition to composition.

The last example is a particularly illustrating one, because it shows how far we can push this process. Here we repeat the same analysis. We notice that the low frequency peak that softens from composition to composition is now very high (notice the scale again). Weight developed everywhere in the Eliashberg function as a consequence of enhancing the Ge content and thus higher T_c was again obtained. Can we proceed? A closer look to the curve shows that the low frequency peak has soften quit a bit. It is slightly to the left from the ideal frequencies. So if we want to have a still higher T_c we have to go back in composition, we have to go back to stochiometry since we are at 25.7% Ge content now. This is a sample which is too rich in Ge. Looking at the whole process we do not expect to get a very different $\alpha^2 F(\omega)$ if we try to go back to stochiometry. But we see that the process is near optimization at this moment and that if we want to rise up T_c further by a substantial amount, we have to go to an entirely new system, a well known fact in this case.

We have seen that the low frequency peak plays the most important role in highering up T_c with changes in the composition. This peak can be associated to the formation of the chains of Nb atoms which are typical to the A–15 structure. the charge distribution around these atoms reveals an almost covalent interaction in the direction of the chains. This very strong interaction is then the clue to the high T_c of these materials.

In conclusion, we have shown in a known example that Eliashberg theory of superconductivity can give valuable information about the way to look for an en-

hancement in T_c in systems where superconductivity is based in the BCS mechanism. There is not general agreement about the mechanism for superconductivity in the new perovskites. Nevertheless, it is not evident form the existing experimental information that for La-based perovskites the electron-phonon interaction can be disregarded as the mechanism that explains superconductivity in these compounds at least as a combined mechanism, as suggested recently [10]. There is not enough experimental information at the moment and in the new perovskites there is an influence of granularity that is to be clarified and eventually separated from the intrinsic mechanism of superconductivity. Both effects could be mixed in at least some of the experimental results.

It is very easy to repeat the calculation for $La_{1.85}Sr_{0.15}$ $Cu0_4$, for example. The Eliashberg function has been calculated by Weber [11] and the thermodynamics that results from strong-coupling theory computed by Carbotte [12]. The different peaks in a measured phonon spectrum have been identified by Rietschel *et al.* [13]. The highest phonons come from the breathing modes of the Cu–0 octahedra. They are located at about 90 meV. The functional derivative of T_c (40 K) with the Eliashberg function has a peak around 7 K T_c (24 meV), as expected and looks exactly the same in shape as the ones in Fig. 1. There is no point in reproducing it again. If we follow the same reasoning as before, we are led to a slightly different conclusion than the one for the Nb–Ge system, but with the same physical content.

To see this, it is important to recall some experimental facts [13]. When neutron scattering experiments are perform at 300 K and repeated at 6 K the only difference between the two spectra is the softening (at 6 K the frequency of the peak is smaller) by about 4 meV of the phonon modes in the plane defined by the nearest-neighbours Cu-atoms. In particular, by the breathing mode of the Cu–0 octahedra. This experimental fact points to the coupling of this mode. It also emphasizes the quasi-two-dimensional character of superconductivity in these compounds. Notice that here we have a different situation from the Nb–Ge system just described, in the sense that *only a part of the phonons that exists in the material do couple.* This is a consequence of the $2D$-character of superconductivity in the new perovskites. Taking this into account we can apply the same criteria from Eliashberg theory in two ways. The first is to set a limit on the T_c attainable and the second on the strength of the coupling. The limit on T_c comes from the fact that the best the system can do is to make its 90 meV mode optimum. In this case 90 meV $= 7\ K\ T_{c\,\max}$ and $T_{c\,\max} = 160\ K$. So we predict that T_c will not be higher than 160 K in systems where the phonons are not higher than 90 meV. This relationship also holds for Y-based perovskites. This is a very suggestive higher limit since no stable and reproducible samples have been reported with a higher T_c. An intensive research stopped at 110–120 K, as it is well known, in Ytrium based perovskites. Does Ytrium help, through the deformation of the lattice, to the better coupling of the breathing mode phonons? The explanation of superconductivity in the new perovskites is certainly an open problem. New mechanisms as polarons, excitons, plasmons, solitons, super-exchange, paramagnons, direct interaction between electrons, etc..., have been proposed. They cannot been ruled out. But the electron-phonon superconductivity has also been invoked in several ways as a possible explanation

(for example when anharmonicity [14] is taken into account). Arguments like "more consistent with experiment" are not to be taken as conclusive proofs, since it is very probably that experiments have still important uncertainties due to sample preparation, reproductibility, proper characterization, etc.... The only conclusive fact is that there are no stable samples with $T_c > 160$ K.

If the electron-phonon interaction has nothing to do with superconductivity in the new perovskites, it is nevertheless striking that the isotopic effect has been detected and that the 90 meV modes in the neutron scattering experiments do soften. All without having nothing to do one with the other?

The second result we want to point out is that the relative value of the functional derivative $\delta\, T_c/\delta\alpha^2 F(\omega)$ at a certain frequency gives qualitative indication of the strength of the coupling. Its low value at 90 meV for the La-based perovskites is indicating that the strength of the electron-phonon coupling at this frequency is medium. A stronger coupling should give a higher T_c than 30 K.

Can we use this information to search for higher-T_c superconductors? If we look at the strengthening of the electron-phonon interaction as the key for high-T_c superconductivity, the enhancement of it leads ultimately to the localization of the electrons in the system, *i.e.*, to a dielectric. So a high-T_c superconductor will be more a dielectric with electrons than a metal with high-energy phonons. This picture applied to the perovskites would lead to the following qualitative image: start from a dielectric (the cupper oxyde). Put it in a crystal potential (perovskite crystal structure) build by some atoms (any lanthanide). Then you get a semiconductor (as La_2CuO_4) by giving some energy to the localized Cu–$d(x^2+y^2)$ and O–p_{xy} electrons. Add impurities (Ba, for example) to mobilize these electrons and you get a very high-phonon (from the dielectric) coupled to electrons: a high-T_c superconductor! The important point being how high the phonons in the starting oxyde are. So one possible way to follow is to look out for oxides with the same octahedrical structure and with higher phonons. One should get a higher-T_c superconductor.

There is a second way with more possibilities: it is to use interfaces to couple high-energy phonons with the appropriate electrons. In this case, the superconducting current would flow parallel to the interface. This last possibility is very appealing because it leaves more freedom to the search. One can do theoretical engineering so to say. Systems like these can be calculated properly not in the free (electron frame), using, for example, the Surface Green Function Matching Method, and such a study is actually in the way. The interesting result would be to set the parameters of the interaction (any one proposed) between the electron and the lattice capable of building Cooper pairs and translate them to be able to choose wisely a proper set of materials to set up an experiment.

As a final comment we draw attention on a very recent publication [15] about the electron-phonon (e–ph) BCS mechanism for Y-based superconducting perovskites. In that work, a very careful analysis of the role of the electron-phonon coupling parameter in predicting T_c is made and it is concluded that Eliashberg theory cannot explain the high-T_c of the Y-based superconducting perovskites. The essential point made, based on approximate equations for T_c, is that a high λ gives a high T_c. This is a known approximate result. The conclusion is that since the λ predicted by the

calculation is very low the corresponding T_c (through Eliashberg theory) is lower compared to experiments. Nevertheless, there is, one point that could be added to the analysis.

The parameter λ denotes an integrated effect weighted with more emphasis at low frequencies. This can be seen directly from the definition since λ is twice the first inverse momentum of the Eliashberg function. In systems where it is experimentally clear that if the electron-phonon interaction plays an important role it will be through high-frequency phonons, λ could not be the best parameter to judge this new situation within Eliashberg theory.

We also want to point out that perovskites have the new feature that the electrons do not couple to all the existing phonons. We feel that the application of Eliashberg theory to the new perovskites is a very subtle point that has not been definitely settled yet.

In conclusion, we have shown that Eliashberg theory can be used to analyze the new La– and *Y*– based perovskites giving results that are not in contradiction with experiments, although the amount of inconsistent experimental results for the same declared sample calls for an absolute need of highly improved fabrication procedures with emphasis on reproductibility. There are, nevertheless aspects of Eliashberg theory that require careful thinking when applied to this new superconductors. We think that it is not set whether Eliashberg theory can or cannot be applied to the new systems. We have set clear limits to its validity by showing the relationship between the frequency of the breathing mode and the highest attainable T_c. It is interesting to see that there is *no* other theory that can predict a limit to T_c under any supposed mechanism. It is also interesting to note that the experimental evidence support the results presented here: there is no superconductor with $T_c >$ 160 K and with a phonon spectrum that ends at frequencies less than 90 meV. We set here an irrefutable way to show that the electron-phonon interaction cannot explain the high-T_c superconductors. The experimental evidence is still consistent with a possible electron-phonon mechanism.

Note added in proofs: W. Pickett in a very extesive review of the electronic structure of the high-temperature oxide superconductors, *Rev. Mod. Phys.* **61** (1989) 433, concludes that for the lanthanum based perovskites, "clearly the electron-phonon interaction is central to the superconducting pairing".

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Abstract. El origen de las altas temperaturas críticas en las nuevas perovsquitas requiere una explicación. En este trabajo nos proponemos mostrar que la teoría de Eliashberg permite un análisis de este importante problema que conduce a respuestas que sugieren posibles caminos a seguir. Vamos a utilizar, como ejemplo, el sistema Nb–Ge con el cual se hicieron los experimentos necesarios para poder aplicar esta teoría. Se puede hacer un análisis en parte con las nuevas perovsquitas con T_c = 40 K, donde el mecanismo electrón-fonón no parece poderse descartar con facilidad al menos como parte de la interacción.