ELSEVIER

Physica C 229 (1994) 396–402

PHYSICA C

Observation of the Holstein shift in high-T_c superconductors with thermal-modulation reflectometry

O.V. Dolgov [a], A.E. Karakozov [b], A.A. Mikhailovsky [b], B.J. Feenstra [c], D. van der Marel [c,*]

[a] P.N. Lebedev Physical Institute, Russian Academy of Science, Moscow 117924, Russian Federation

[b] L.F. Vereschagin Institute for High Pressure Physics, Troitsk, Russian Federation

[c] Materials Science Center, Solid State Physics Laboratory, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received 2 April 1994; revised manuscript received 15 June 1994

Abstract

We use the experimental technique of thermal-modulation reflectometry to study the relatively small temperature dependence of the optical conductivity of superconductors. Due to a large cancellation of systematic errors, this technique is shown to be a very sensitive probe of small changes in reflectivity. We analyze thermal-modulation reflection spectra of single crystals and epitaxially grown thin films of $YBa_2Cu_3O_{7-\delta}$ and obtain the $\alpha_t r^2 F(\omega)$ function in the normal state, as well as the superconductivity-induced changes in reflectivity. We present detailed model calculations, based on the Eliashberg–Migdal extension of the BCS model, which show good qualitative and quantitative agreement with the experimental spectra.

1. Introduction

Optical spectroscopy in the infrared region provides a valuable tool to study low-energy excitations in high-T_c superconductors. In principle such measurements can provide information about the superconducting energy gap (if any) and the pairing mechanism. A lot of discussion is still focussed on the problem of how to distinguish electronic contributions from those which are due to phonons, and to what extent these two are coupled. The latter deserves special attention, because in the conventional superconductors electron–phonon coupling is believed to be responsible for superconductivity. While the role of electron–phonon coupling is not very clear in the new high-T_c materials, there exists a tendency in the theoretical community to consider conventional coupling mechanisms, such as electron–phonon, as a necessary ingredient to obtain pairing. It is not yet clear, however, whether an exceptionally large electro–phonon coupling is really required, or whether a small germ suffices, which is then further "boosted" by other mechanisms such as interlayer pairing (as was recently proposed by Anderson [1]). This uncertainty emphasizes the importance of a proper understanding of electron–phonon coupling in these materials if we want to make progress towards a theory of high-T_c superconductivity which is of practical importance, e.g. is able to predict T_c for new compounds. Although many data of high quality have been obtained on a wide variety of cuprate high-T_c superconductors, it has turned out to be difficult to obtain a clear interpretation of these data. In particular, there have been many papers where the observation of a "clean" gap has been claimed, but closer inspection reveals that there is a considerable amount of residual absorptivity at energies below the presumed gap. Some of the difficulties are connected with

* Corresponding author.

0921-4534/94/$07.00
SSDI 0921-4534(94)00395-V

experimental problems concerning the complicated structure of such systems, but others are related to the theoretical interpretation of the results obtained. Two examples are that the value these gaps would have is far too high to be compatible with a simple BCS picture, and the position of these features does not appear to shift to zero frequency if $T \to T_c$. Instead a gradual filling of the gap region is observed with a change of slope of the intensity in this region at the phase transition, which can be fitted in a phenomenological way using a two-fluid description of the superconducting state.

In the conventional theory superconductivity is a consequence of electron pairing mediated by the exchange of the Bose-like excitations. This pairing leads to the appearance of an energy gap and hence to zero absorption for frequencies less than 2Δ. In the optical data it is possible to determine this threshold by measuring the departure of the reflectivity from unity, or of the absorptivity from zero. The most informative value is the optical conductivity (σ). But in order to calculate σ it is necessary to determine with great accuracy small departures from 100% reflectivity, followed by a Kramers–Kronig analysis to obtain the phase of the reflectivity. When the absolute reflectivity is close to 100% the progression of experimental errors in this procedure often leads to large uncertainties in the conductivity.

For experimental reasons 2Δ was determined in conventional superconductors as a maximum of the ratio of the reflectivity in the SC state to the normal state. For HTS there are several difficulties when one tries to apply this procedure due the high critical temperature T_c itself. Between zero temperature and T_c some intrinsic changes in the electronic subsystem occur, due to which we have practically two different substances at low (helium) and normal-state temperatures. This is even more important if the mechanism of pairing is of an electronic nature.

2. Thermal-modulation reflectometry

Another method of the determination of the energy gap has been used by Abel et al. [2]. It provides a possible way to avoid some of the aforementioned difficulties (e.g. problems with the absolute value of reflectivity and Kramers–Kronig transformations). Abel et al. determined the ratio of optical reflectivities at two close temperatures $R(\omega, T)/R(\omega, T+\delta T)$, and the maximum of this ratio was ascribed to the superconducting energy gap $2\Delta(T)$. This feature reflects the fact that the main change below T_c is due to the decrease of Δ in the single-particle excitation spectrum. However, in real superconductors the situation is more complicated. First, for $T>0$ the gap itself is not well defined. Second, we have a strong temperature dependence of the number of thermally excited Bose-like quasi-particles. As we shall see below, this is the dominating effect, and gives us a possibility to extract information about the spectrum of these intermediate bosons. The third complication is connected to the so called Holstein shift. The optical conductivity contains contributions from the intermediate bosons which are responsible for the pairing *because* they are coupled to the electron–hole excitations (boson-assisted conductivity, see e.g. Refs. [3] and [4]). The difference between the normal and the superconducting state is the following: A threshold point of an absorption which in the former case takes place at the characteristic boson frequency Ω_0 should in the latter case be shifted to $\Omega_0+2\Delta$. This effect was observed in conventional superconductors and played an important role in establishing the phonon-mediated nature of superconductivity in these systems [5,6]. However, the absence of such a shift in the reflectivity spectra of high-T_c superconductors is one of the most important objections against the conventional mechanism of superconductivity in these compounds [7,8]. The thermo-modulation method, in which the ratio of reflectivities at two close temperatures is analyzed [2], gives the possibility to observe the boson anomalies in the normal as well as in the superconducting state. In the present paper we make a detailed comparison between model calculations based on strong-coupling theory, and experimental thermo-modulation reflection spectra. The data used in the present analysis are in good agreement with those obtained by Abel et al., but cover a wider range of frequencies and temperatures.

The main advantage of measurements of $R(\omega, T)/R(\omega, T+\delta T)$ between two close temperatures is that all thermal effects connected with extrinsic factors (e.g. the experimental setup, spurious signals) are compensated and the ration reflects only the temperature dependence of the occupation numbers of the bosonic and fermionic excitations. If the change of temperature $\delta T \ll T$, it is possible to expand

$$R(\omega, T)/R(\omega, T+\delta T) = 1 + r(\omega, T)\delta T . \tag{1}$$

From the expression for the reflectivity at normal incidence $R = |(1-\sqrt{\epsilon})/(1+\sqrt{\epsilon})|^2$ one obtains the following exact expression for the thermo-reflectance coefficient:

$$r(\omega, T) \equiv -\partial \ln R(\omega, T)/\partial T$$
$$= -2\,\mathrm{Re}\left[\frac{\partial\epsilon/\partial T}{(\epsilon-1)\sqrt{\epsilon}}\right]. \tag{2}$$

Although in the comparison which we will make to experimental optical data we will use numerical calculations based on the full solution of the Eliashberg equations, we will make some further approximations in order to demonstrate that $r(\omega, T)$ reflects the $\alpha_{\mathrm{tr}}^2 F$ function. We first notice, that for a good metal in the frequency region under consideration $(\omega \ll \omega_{\mathrm{p}})$ $|\epsilon'| \gg 1$, so that we may write $r(\omega, T) = 4\,\mathrm{Re}\,\partial(\epsilon^{-1/2})/\partial T$. As can be seen from Fig. 8 of Ref. [11] $0.25 < \epsilon''/\epsilon' < 0.4$ for the relevant frequency range in the superconducting state. Although in the next section we will make a comparison between experiment and theory using the exact expression for the thermo-reflection (Eq. (2)), in the present qualitative discussion we only consider the "clean" limit, where $(\epsilon''/\epsilon') = (\omega\tau)^{-1}$ may be treated as a small parameter in a Taylor series expansion. The leading order of this expansion is

$$r(\omega, T) \approx 2\frac{\partial}{\partial T}\frac{\epsilon''}{|\epsilon'|^{3/2}}. \tag{3}$$

For the description of the dielectric function in the normal state we use the extended Drude expression [9]

$$\epsilon(\omega, T) = \epsilon_\infty - \frac{\omega_{\mathrm{p}}^2/\omega^2}{m^*(\omega)/m + \mathrm{i}/(\omega\tau(\omega))}. \tag{4}$$

We will here make the approximation that the main temperature dependence enters through the parameter $\tau(\omega)$. As we consider here the range of frequencies where $\omega\tau \gg 1$, we obtain the simple expression

$$r(\omega, T) = \frac{2}{\omega_{\mathrm{p}}}\frac{\partial\tau^{-1}}{\partial T}. \tag{5}$$

As is shown in the Appendix, for sufficiently low frequencies the temperature derivative of the optical scattering rate is proportional to the transport spectral function, whereas at high frequencies it is proportional to λ_{tr}, so that

$$r(\omega, T) = \frac{4\pi}{\omega_{\mathrm{p}}}\begin{cases}\lambda_{\mathrm{tr}} & (T \gg \Omega_0)\\ \dfrac{2\pi^2 T}{3\omega}\alpha_{\mathrm{tr}}^2(\omega)F(\omega) & (T \ll \Omega_0)\end{cases}. \tag{6}$$

So we see that thermal-modulation reflectometry can provide rather direct experimental information on the transport spectral function.

In the superconducting state it is possible to obtain a useful expression in the region where $-\epsilon' \simeq c^2/(\omega^2\lambda_{\mathrm{L}}^2) \gg 4\pi\sigma_1(\omega, T)/\omega$ (i.e., when $R \simeq 1$), where $\sigma_1 = \omega\epsilon''/(4\pi)$ is the real part of the optical conductivity. Here λ_{L} is the London penetration depth. In this case

$$r(\omega, T) = 8\pi c^{-3}\lambda_{\mathrm{L}}^3\omega^2\frac{\partial\sigma_1(\omega, T)}{\partial T}. \tag{7}$$

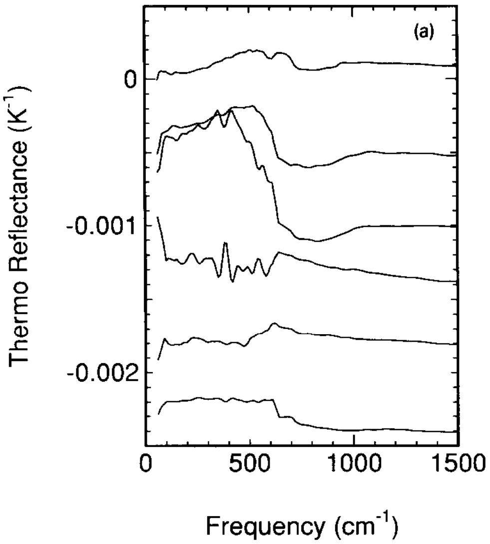
In the Appendix we show that in the superconducting state the dominant term in $\partial\sigma_1(\omega, T)/\partial T$ is proportional to $\alpha_{\mathrm{tr}}^2 F(\omega - 2\Delta)$. As a result we obtain, disregarding the slowly varying term

$$r(\omega, T) = \frac{8\pi^3\omega_{\mathrm{p}}^2\lambda_{\mathrm{L}}^3 T}{3c^3}\alpha_{\mathrm{tr}}^2(\omega-2\Delta)F(\omega-2\Delta). \tag{8}$$

At intermediate temperatures the dielectric function can sometimes be approximated with the two-fluid interpolation formula $\epsilon(\omega, T) = \epsilon_{\mathrm{s}} f_{\mathrm{s}}(T) + \epsilon_{\mathrm{n}}(1 - f_{\mathrm{s}}(T))$, as was supported experimentally [11] for $YBa_2Cu_2O_{7-\delta}$ and theoretically in the case of strong or intermediate coupling [12], where $\epsilon_{\mathrm{s}}(\omega)$ and $\epsilon_{\mathrm{n}}(\omega)$ are the dielectric functions at $T=0$, and at $T \geq T_{\mathrm{c}}$, respectively. The function $f_{\mathrm{s}}(T)$ is proportional to the number of superconducting electrons and is assumed to be of the form $f_{\mathrm{s}}(T) = 1 - (T/T_{\mathrm{c}})^\nu$ where ν is some exponent (usually $\nu = 4$). For $T < T_{\mathrm{c}}$ we see that $r(\omega, T) \propto \mathrm{Re}[\sigma_{\mathrm{n}}(\omega) - \sigma_{\mathrm{s}}(\omega)]$ and has its maximal amplitude directly below T_{c}.

3. Comparison of experimental data with strong-coupling calculations

In Fig. 1(a) the experimental values of the thermo-reflectance coefficient $r(\omega, T)$ are displayed for an



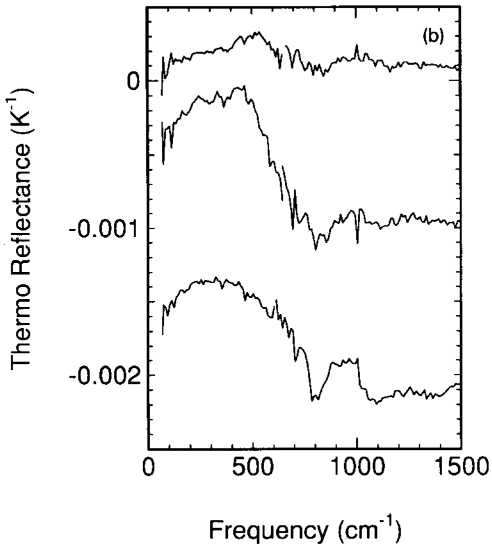


Fig. 1. (a) Experimental $r(\omega, T)$ with $E \perp c$ for an epitaxial thin film of $YBa_2Cu_3O_{7-\delta}$. From top to bottom: T=35, 55, 75, 95, 115 and 135 K. The curves have been shifted vertically with 0, −0.0005, −0.0010 K^{-1}, etc. (b) The same for a single crystal. Temperatures are 35, 80 and 125 K. Vertical offsets have been given of 0, −0.001 and −0.002 K^{-1}.

ab-oriented thin film of $YBa_2Cu_3O_{7-\delta}$ with $T_c = 90$ K [11] for temperatures between 30 K and 140 K. The ratios were calculated from data differing by 10 K. We see a feature in the frequency region $\omega \leq 1000$ cm^{-1} both in the normal state and in the superconducting state. We made a similar analysis of the data obtained by Bauer on a single crystal of $YBa_2Cu_3O_{6.8}$ with a T_c of 81–86 K [14]. As only reflectivity data at 10, 60, 100 and 150 K were taken, the ratios

$$\frac{2}{T_2 - T_1} \frac{R(T_1) - R(T_2)}{R(T_1) + R(T_2)}$$

(displayed in Fig. 1(b)) are calculated for the pairs (T_1, T_2) = (10, 60), (60, 100) and (100, 150). Although one expects deviations from a pure thermal derivative in this case, the thermal-modulation spectra obtained from both sets of data are actually quite similar. The origin of the larger value of r between 100 K and 150 K in Bauer's data is not clear, and may be due to the lower oxygen concentration with a T_c of 80–85 K in this sample. In the normal state all features end at the frequencies near 700 cm^{-1}, which corresponds to the range of phonon frequencies for these materials. According to expression (6) the shape of $r(\omega, T)$ should be proportional to the spectrum of intermediate phonons $\alpha_{\rm tr}^2 F(\omega)$. This gives us the possibility to speak about the intermediate-boson contribution to the optical properties of high-T_c systems.

Let us first calculate the thermo-modulation spectra using the weak-coupling BCS model in the clear-limit, either assuming a single gap at 220 cm^{-1} (Fig. 2(a)) or a distribution of gaps between 0 and 500 cm^{-1} (Fig. 2b)). We see, that the calculated $r(\omega, T)$ has only one feature corresponding to the energy gap. Also the calculated thermomodulation effect on the reflectivity is much larger than the experimental values.

To obtain a better understanding of these features we carried out model calculations of the reflectivity assuming an $\alpha^2 F$ function with a single broad peak at $\omega_0 = 350$ cm^{-1}, the constant of interaction being $\lambda = 1.5$, and the bare $\omega_p = 3$ eV, which gives a critical temperature $T_c = 87$ K. This shape of $\alpha^2 F(\omega)$ was used in Ref. [13]. These parameters lead to a linear dependence of the resistivity in the normal state, with a slope that corresponds to experimental values [15]. To match the 164 K data it is either necessary to take a larger ω_0 or a larger λ (≈ 2.5). The results are shown in Fig. 3.

According to expression (8), for $T \ll T_c$ the spectrum of the intermediate bosons should be shifted by 2Δ. The experimental data indeed show such a shift and make it possible to estimate the value of 2Δ (if Δ_k is actually a distribution of gap values due to e.g.

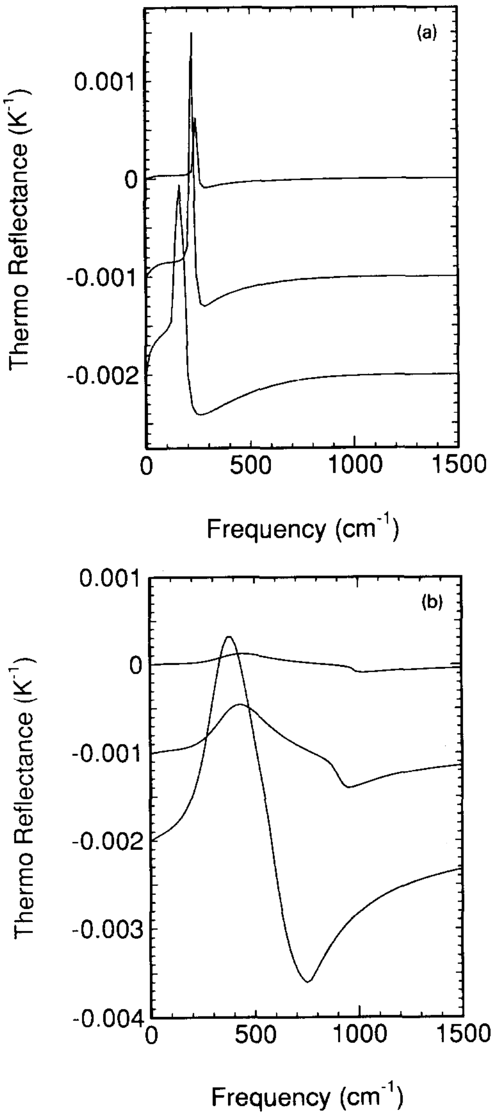


Fig. 2. (a) Theoretical calculation of $r(\omega, T)$ based on the BCS model ($2\Delta = 3.5\ k_B T_c$) using the method of Ref. [16]. Temperatures are 35, 55 and 75 K from top to bottom. Vertical offsets have been given of 0, -0.001, and -0.002 K^{-1}. (b) Theoretical calculation of $r(\omega, T)$ based on a BCS-like model with a gap distributed between 0 and $8k_B T_c$. Temperatures and offsets are as in Fig. 2(a).

anisotropic pairing, the shift corresponds to a gap value averaged over the Fermi surface) to be 250 to 300 cm^{-1}, corresponding to a ratio $2\Delta/T_c \approx 4$ to 5. It is interesting to note the negative contribution to $r(\omega, T)$ above $2\Delta + \Omega$, which is a consequence of the modification of the optical conductivity (second term in

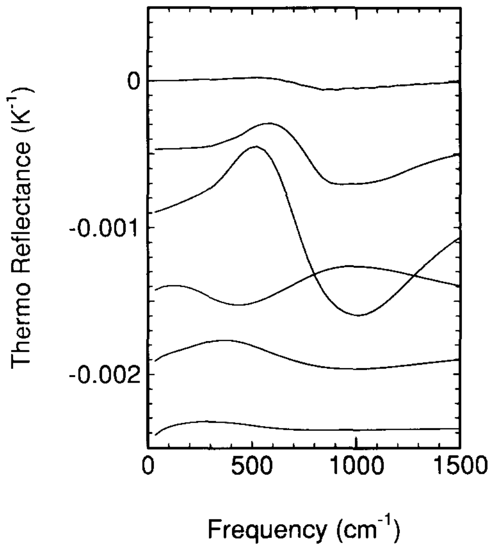


Fig. 3. Theoretical calculation of $r(\omega, T)$ based on the strong-coupling formalism with parameters as explained in the text. From top to bottom: T=35, 55, 75, 95, 115 and 125 K. The curves have been shifted vertically with 0, -0.0005, -0.0010 K^{-1}, etc.

Eq. (14)). At intermediate temperatures the ratio $r(\omega, T)$ behaves according to the two-fluid model and reaches a maximal amplitude just below T_c.

4. Conclusions

We demonstrate that thermal-modulation reflectometry can be used to record small changes in reflectivity of superconductors, even if the reflectivity itself is close to 100%. We observe that the thermal modulations of superconducting $YBa_2Cu_3O_{7-\delta}$ are quite small, but well reproducible from sample to sample. Although the observed effects are much smaller than results of a weak-coupling BCS-type calculation in the clean limit, qualitatively good agreement with a strong-coupling type model calculation is obtained, where $\lambda = 1.5$, and $\omega_p = 3$ eV is assumed, and an $\alpha^2 F$ function with a single broad peak at 350 cm^{-1} is taken.

Acknowledgements

This work was completed with financial aid from the Nederlandse Organisatie voor Wetenschappelijk

Onderzoek. We thank L. Genzel, and M. Bauer for making their data files available in digital form.

Appendix A

Normal state

Let us first consider the reflectance in the normal state. The temperature dependence of the optical-scattering rate can be expressed using the reaction of Ref. [10] (valid for $\omega\tau \gg 1$)

$$\tau(\omega,T)^{-1} = \frac{\pi}{\omega}\int_0^\infty d\Omega \alpha_{\rm tr}^2(\Omega)F(\Omega)\left[2\omega\coth\left(\frac{\Omega}{2T}\right) + (\omega-\Omega)\coth\left(\frac{\omega-\Omega}{2T}\right) - (\omega+\Omega)\coth\left(\frac{\omega+\Omega}{2T}\right)\right], \quad (9)$$

where $\alpha_{\rm tr}^2(\omega)F(\omega)$ is a transport spectral function of the electron–boson interaction

$$\alpha_{\rm tr}^2(\omega)F(\omega) = \frac{N(0)}{4v_{\rm F}} \langle\langle |M_{kk'}|^2(V_k - V_{k'})^2 \delta(\Omega_{k-k'}-\omega)\rangle\rangle, \quad (10)$$

where Ω and M are an intermediate-boson frequency and a matrix element, and $\langle\langle ... \rangle\rangle$ denotes an average over the Fermi surface. In the limiting cases, where the temperatures are either much smaller or much larger than the characteristic frequency Ω_0, we have

$$\tau(\omega,T)^{-1} = \begin{cases} 4\pi T \int_0^\infty d(\ln\Omega)\alpha_{\rm tr}^2(\Omega)F(\Omega) = 2\pi\lambda_{\rm tr}T & (T \gg \Omega_0), \\ \frac{2\pi}{\omega}\int_0^\infty d\Omega\, \alpha_{\rm tr}^2(\Omega)F(\Omega)(\omega-\Omega) & \\ \quad + \frac{2\pi^3}{3\omega}T^2\alpha_{\rm tr}^2(\omega)F(\omega) & (T \ll \Omega_0). \end{cases} \quad (11)$$

The first term has been previously obtained by Allen [4]. The first derivative with respect to temperature becomes

$$\frac{\partial\tau(\omega,T)^{-1}}{\partial T} = \begin{cases} 2\pi\lambda_{\rm tr} & (T \gg \Omega_0), \\ \frac{4\pi^3 T}{3\omega}\alpha_{\rm tr}^2(\omega)F(\omega) & (T \ll \Omega_0). \end{cases} \quad (12)$$

Appendix B

Superconducting state

For $T \ll T_c$ the expression for the boson-assisted conductivity was obtained by Allen [4]:

$$\sigma_1(\omega,T) = \frac{\pi e^2}{6\omega^2}\langle\langle |M_{kk'}|^2(V_k - V_{k'})^2 f_k(1-f_{k'}) \times\left(1-\frac{\epsilon_k\epsilon_{k'} - \Delta_k\Delta_{k'}}{E_kE_{k'}}\right)\delta(E_k + E_{k'} + \Omega_{k-k'} - \omega)\rangle\rangle.$$

Here $E_k = (\epsilon_k^2 + \Delta_k^2)^{1/2}$ is a quasiparticle spectrum, Δ_k is the superconducting gap and f_k is the Fermi distribution. For low temperatures $T \ll \Delta$ it is possible to neglect the temperature dependence of the gap, and we obtain

$$\frac{\partial\sigma_1(\omega,T)}{\partial T} = \left(\frac{\pi e^2}{6\omega^2}\frac{2\pi^2 nT}{m}\right)\left\{-4\alpha_{\rm tr}^2F(\omega-2\Delta) + \int_0^{\omega-2\Delta} d\Omega\alpha_{\rm tr}^2F(\Omega)\frac{\sqrt{(\omega-\Omega)(\omega-\Omega-2\Delta)}}{\Delta(\omega-\Omega-\Delta)}\right\}. \quad (14)$$

The first term is proportional to the Eliashberg function $\alpha_{\rm tr}^2(\omega)F(\omega)$ shifted by 2Δ (Holstein shift). The second term is weakly varying with frequency and is a consequence of a modification of the conductivity at $\omega > 2\Delta + \Omega$.

References

[1] S. Chakravarty, A. Sudbo, P.W. Anderson and S. Strong, Science 261 (1993) 337.

[2] E.V. Abel, V.S. Bagaev, D.N. Basov, A.F. Plotnikov, A.G. Poiarkov and V.G. Shutov, BRUKER Report 1 (1991) 21; E.V. Abel, V.S. Bagaev, D.N. Basov, A.F. Plotnikov, A.G.

Poiarkov and V.G. Shutov, Pisma Zh. Eksp. Teor. Phiz. 47 (1988) 144 (JEPT Lett. 47 (1988));
E.V. Abel, V.S. Bagaev, D.N. Basov, A.F. Plotnikov, A.G. Poiarkov and V.G. Shutov, Solid State Commun. 75 (1990) 507.
[3] T. Holstein, Phys. Rev. 96 (1954) 535;
T. Holstein, Ann. Phys. (N.Y.) 29 (1964) 410.
[4] P.B. Allen, Phys. Rev. B 3 (1971) 305.
[5] R.R. Joyce and P.L. Richards, Phys. Rev. Lett. 24 (1970) 1007.
[6] B. Farnworth and T. Timusk, Phys. Rev. B 10 (1974) 2799; 14 (1976) 5119.
[7] Tanner and T. Timusk, in: Physical Properties of High Temperature Superconductors, part 3, ed. D.M. Ginsberg (World Scientific, Singapore, 1992).
[8] Z. Schlesinger, R.T. Collins, F. Hotzberg, C. Feild, N.E. Bickers and S.J. Scalapino, Nature (London) 343 (1990) 242.
[9] J.W. Allen and J.C. Mikkelsen, Phys. Rev. B 15 (1977) 2952.
[10] S.V. Shulga, O.V. Dolgov and E.G. Maksimov, Physica C 178 (1991) 266.
[11] D. van der Marel, H.U. Habermeier, D. Heitmann, W. König and A. Wittlin, Physica C 176 (1991) 1.
[12] A.A. Mikhaikovsky and S.V. Shulga et al., Solid State Commun. 80 (1991) 511.
[13] A.E. Karakozov, E.G. Maksimov and A.A. Mikhailovsky, Sov. Phys. JETP 75 (1992) 70.
[14] M. Bauer, Ph.D. thesis, University of Würzburg (1990).
[15] I.I. Mazin and O.V. Dolgov, Phys. Rev. B 45 (1992) 2509.
[16] W. Zimmermann, Diplom Arbeit, University of Bayreuth (1983);
W. Zimmermann, E.H. Brandt, M. Bauer, E. Seider and L. Genzel, Physica C 108 (1991) 99.