Role of anharmonicity in the electronic heat capacity of superconductors

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Abstract. The role of anharmonicity in the electronic heat capacity (EHC) of high temperature superconductors (HTS) has been investigated via electron density of state (EDOS) using quantum dynamical approach. The EDOS may be obtained using correlation function with the help of Zubarev double time temperature dependent electron Green’s functions (GF) via a generalized Hamiltonian which consists of (i) unperturbed electron, (ii) unperturbed phonon, (iii) electron-phonon, (iv) anharmonic and (v) defect interactions. The model Hamiltonian includes the force constant changes and mass difference caused by the impurities along with the effects of cubic anharmonicity reveals some striking features of EHC of HTS.

1. Introduction

One of the most important equilibrium thermodynamic properties of a crystal is the heat capacity. The measurements of EHC have been widely studied techniques. Experimental observations [1-3] reveal that EHC is highly sensitive at low temperatures. Some of the theoretician [4-7] studied the low temperature impurity induced heat capacity. While the heat capacity of superconducting material at low temperature have been measured by a large number of authors [8-10]. Also a number of reviews of the thermal properties of high temperature superconductors have been given by many authors [11-16]. But none of these workers have considered the anharmonic effects on heat capacity. Only a few of them [17-26] have worked on anharmonic effects, but even that not in a convincing way. They have not used the effect of defects and anharmonicity in an explicit manner. It is mentioned here that defects play an important role in the low temperature region in the analysis of EHC. Also the effect of anharmonic phonon field does not vanish even at absolute zero of temperature and the impurities [23] in a crystal radically change the energy scenario. The theories of EHC proposed till now, however, are more or less based on the free electron theory and could not explain the complete phenomenon [24-28]. There have been several attempts to explain heat capacity of high $T_c$ copper oxides superconductors using a Van Hove singularity in the EDOS [29-36]. In some of these approaches electron-phonon model is used.

In the present theory electronic heat capacity has been developed on the basis of quantum dynamics of electrons [37-38]. It is observed that the electron-phonon coupling plays a crucial role in determining EHC. The change in EHC due to substitutional impurities by the effect of force constant only has been described by many workers [39-41]. But the present theory reveals that this change depends not only on the mass change parameters and the force constant changes, but also on the cross...
terms of third and fourth order anharmonic parameters with the defect terms. In this scenario we considered an interacting system of electron-phonon fields instead of considering a container of free electron gas or electrons only [42].

2. Formulation of the problem
Our approach is based on the quantum dynamics via double-time thermal Green’s functions method. The heat capacity may be obtained from crystal energy and DOS [2, 43] without using any quasiharmonic approximation. The shortcoming of the quasiharmonic approximation in the evaluation of thermodynamic properties has been discussed by Barron [44]. Temperature dependence DOS is also one of the important feature of this work.
In the formulation of EHC, the total energy of the system may be obtained in the form [45]

\[ E = E_0 + \left( \pi^2 / 6 \right) (k_B T)^2 N(\epsilon, T) \]  

(1)

where \( E_0 = \int_0^\epsilon N(\epsilon, T) d\epsilon \), is the total energy at \( 0^0K \) with \( \epsilon_f \) is the Fermi energy. As EDOS cannot be taken independent of temperature, EHC can be evaluated by taking the temperature derivative of eqn. (1) in the following form,

\[ C_{el}(T) = \frac{\partial E}{\partial T} = C_{el}^{(1)}(T) + C_{el}^{(2)}(T) \]  

(2)

where

\[ C_{el}^{(1)}(T) = \left( \pi^2 / 3 \right) k_B^2 T N(\epsilon, T) \]  

(3)

\[ C_{el}^{(2)}(T) = \left( \pi^2 / 6 \right) (k_B T)^2 \frac{\partial}{\partial T} N(\epsilon, T). \]  

(4)
The electron density of states \((N(\epsilon, T))\) can be described in the form of Lehman representation as [37, 46]

\[ N(\epsilon, T) = -\sum_k \text{Im} G_{q,\alpha}(q, \epsilon) \]  

(5)

where \( G_{q,\alpha}(q, \epsilon) = \langle \{ b_{q,\alpha}^+(t) b_{q,\alpha}^-(t') \} \rangle = -i\theta(t, t') \langle \{ b_{q,\alpha}^+(t) b_{q,\alpha}^-(t') \} \rangle \) is the electron Green’s function with \( b_{q}^+(b_{q}^-) \) are electron annihilation (creation) operators with wave vector \( \alpha \).

3. Quantum dynamics
The quantum dynamics of electron system is investigated with the help of an almost complete Hamiltonian which includes the effects of electron-phonon, defects, anharmonicities and interference of thereof. The double time temperature dependent Green’s functions for electrons and phonons have been obtained in the case of layered compounds. Having obtained the correlation function [47] via Green’s function we are able to obtain the electron and phonon self energies, electron and phonon density of states etc, which enable us to study the various physical properties of layered compounds in the framework of many body theory.

3.1. The Hamiltonian and Electron Green's Function
The complete Hamiltonian (with out BCS) for the said problem may be expressed as

\[ H = H_{eo} + H_{po} + H_{qv} + H_A + H_B \]  

(6)

The details of the contributions to the Hamiltonian are given in references elsewhere [37, 46, 48-49]. The double time temperature dependent Green’s function can be evaluated via Hamiltonian (6) using equation of motion technique [47] and Dyson’s equation [48, 50] in the final form as

\[ G(q, \epsilon) = (2\pi)^{-1} (3\epsilon^N + \epsilon^C) \delta_{q,\alpha=q',\sigma} \left[ \epsilon^2 - \epsilon_{q,\alpha}^2 + (3\epsilon^N + \epsilon^C) \Gamma(q, \epsilon) \right]^{-1} \]  

(7)
where $\varepsilon^N$ and $\varepsilon^C$ are the normal energy and Cooper pair energy and $\tilde{\varepsilon}_q$ is the energy of renormalize mode which takes the form

$$\tilde{\varepsilon}_q^2 = (3\varepsilon^N + \varepsilon^C)^2 - \alpha f(2\pi) - (3\varepsilon^N + \varepsilon^C)^{-1}\sum_{q'}(g_{k} + g_{k'})\beta f(2\pi)$$

(8)

Also $\tilde{\varepsilon}_q^2 = \tilde{\varepsilon}_q^2 + (3\varepsilon^N + \varepsilon^C)\Delta(q,\varepsilon)$ is the energy of perturbed mode. Here $\Delta^{(e)}(q,\varepsilon)$ and $\Gamma^{(e)}(q,\varepsilon)$ indicate electron energy shift and line width of electron [48].

3.2. Electron Density of States (EDOS)

The evaluation of energy spectrum or density of states for electron is basic building block of dynamical properties of crystalline solids. The electron density of states in the high temperature superconductors can be explored with the help of Green’s functions (7) in the form as

$$N^{(e)}(\varepsilon,T) = \frac{(3\varepsilon^N + \varepsilon^C)^2\Gamma(q,\varepsilon)}{2\pi[(\varepsilon^N + \varepsilon^C)^2 - (3\varepsilon^N + \varepsilon^C)^2\Gamma^2(kq,\varepsilon)]}$$

(9)

For small value of $\Gamma(q,\varepsilon)$ equation (9) may be written as

$$N^{(e)}(\varepsilon,T) = \sum_m N^{(e)}_m(\varepsilon,T) = \sum_m \frac{(3\varepsilon^N + \varepsilon^C)^2\Gamma_m(q,\varepsilon)}{2\pi[(\varepsilon^N + \varepsilon^C)^2 - (3\varepsilon^N + \varepsilon^C)^2\Gamma^2_m(kq,\varepsilon)]}$$

(10)

with $m = ep, 3A, 4A, D$. The various contributions to EDOS now can be summarized as [48,50]:

$$N^{(e)}_{ep}(\varepsilon,T) = -\sum_{k,q}G_{k,k}^2(\varepsilon^2 - \tilde{\varepsilon}_q^2)^{-2}\left\{8\tilde{\xi}(\varepsilon)N_{q\sigma} \left[4\tilde{\xi}_k^{-1}(3\varepsilon^N + \varepsilon^C)^2 - \varepsilon_k^2 - \varepsilon_{k-k} \tilde{\varepsilon}_k\right] \right\}$$

(11a)

$$= \left[\sum_{k,q}G_{k,k}^2(\varepsilon^2 - \tilde{\varepsilon}_q^2)^{-2}\left\{8\tilde{\xi}_k^{-1}(3\varepsilon^N + \varepsilon^C)^2 - \varepsilon_k^2 - \varepsilon_{k-k} \tilde{\varepsilon}_k\right\} \right]$$

(11b)

$$N^{(e)}_{3A}(\varepsilon,T) = 288\sum_{k,q,k_1\neq k_2}V_{3}(k_1,k_2,-k)G_{k,k}^2(\varepsilon^2 - \tilde{\varepsilon}_q^2)^{-2}\left\{\eta_{12}\tilde{\xi}(\varepsilon)N_{q\sigma} \left[S_{\alpha\gamma} \tilde{\varepsilon}_\gamma^{-1} \right] \right\}$$

(11c)

$$N^{(e)}_{4A}(\varepsilon,T) = 2^9\sum_{k,q,k_1\neq k_2}V_{4}(k_1,k_2,k_3,-k)G_{k,k}^2(\varepsilon^2 - \tilde{\varepsilon}_q^2)^{-2}\left\{\tilde{\xi}(\varepsilon) \left[S_{\alpha\beta} \tilde{\varepsilon}_\beta^{-1} \right] \right\}$$

(11d)

$$N^{(e)}_{D}(\varepsilon,T) = 2^6\sum_{k,q,k_1\neq k_2}D(k_1,-k)G_{k,k}^2(\varepsilon^2 - \tilde{\varepsilon}_q^2)^{-2}\left\{2\tilde{\xi}(\varepsilon)N_{q\sigma} \left[\eta_{12}N_{q\sigma} \left[S_{\alpha\gamma} \tilde{\varepsilon}_\gamma^{-1} \right] \right] \right\}$$

The details of various symbol used in eqns.(9-11) are given in references[50-51].

4. Analysis of Electronic Heat Capacity

Using the various contributions of EDOS (eqn. 11) in eqn. 2 and eqn. 3, we can obtain the total EHC with various contributions in the form
$$C_{el}^{EP} = \pi \gamma \sum_{k,k'} G_{k,k'}^2 \left\{ X(\bar{e}_k, \bar{\gamma}_q) \bar{e}_k \bar{e}_k^{-1} \left[ 4T N_{\bar{\rho}_\sigma}(\varepsilon_k^4 - 4 \varepsilon_k^2 \varepsilon_{NC}^2) + k_B^{-1}(\varepsilon_k^4 - 4 \varepsilon_k^2 \varepsilon_{NC}^2) \right] \right. \\
\times \left. (f^n + f^C) \right) + X(\bar{e}_{NC}^2, \bar{\gamma}_q) \bar{e}_{NC}^2 \left[ 4T (\varepsilon_k^2 n_k + 4 \varepsilon_k \bar{\eta}_k \varepsilon_{NC}^{-1} + \bar{\eta}_k \varepsilon_{NC}^2) \right] \\
+ k_B^{-1} \bar{e}_k \bar{e}_k^{-1} \left( \varepsilon_k^3 + 4 \varepsilon_k^2 \varepsilon_{NC}^2 + \bar{\eta}_k \varepsilon_{NC}^2 (n_k^2 - 1) \right) \right\} \\
C_{el}^{3AE} = 36 \pi \gamma \sum_{k,k',k_1,k_2} G_{k,k',k_1,k_2}^2 \left\{ X(\bar{e}_{\alpha \beta}, \bar{\gamma}_q) \bar{e}_{\alpha \beta}^2 \eta_{12} \right. \\
\times \left[ 4T N_{\bar{\rho}_\sigma} S_{\alpha \beta} + k_B^{-1} \left[ N_{\bar{\rho}_\sigma} \bar{\xi}^+ + S_{\alpha \beta} (f^n + f^C) \right] \right] + X(\bar{e}_{\alpha}, \bar{\gamma}_q) \bar{e}_{\alpha}^2 \eta_{12} \\
\times \left[ 4T N_{\bar{\rho}_\sigma} S_{\alpha \beta} + k_B^{-1} \left[ N_{\bar{\rho}_\sigma} \bar{\xi}^- + S_{\alpha \beta} (f^n + f^C) \right] \right] + 2X(\bar{e}_{NC}, \bar{\gamma}_q) \bar{e}_{NC}^2 \\
\times \left[ 4T n_k n_k + k_B^{-1} (n_{k_1} n_{k_2} n_{12} - \alpha_{12}) \right] \right\} \\
C_{el}^{4AE} = 192 \pi \gamma \sum_{k,k',k_1} G_{k,k',k_1}^2 \left\{ X(\bar{e}_{\alpha \beta}, \bar{\gamma}_q) \bar{e}_{\alpha \beta}^2 \eta_{123} \right. \\
\times \left[ 4T N_{\bar{\rho}_\sigma} S_{\alpha \beta} + k_B^{-1} \left[ N_{\bar{\rho}_\sigma} \bar{\xi}^+ + S_{\alpha \beta} (f^n + f^C) \right] \right] + X(\bar{e}_{\alpha \beta}, \bar{\gamma}_q) \\
\times \bar{e}_{\alpha \beta}^2 \eta_{123} \left[ 4T N_{\bar{\rho}_\sigma} S_{\alpha \beta} + k_B^{-1} \left[ N_{\bar{\rho}_\sigma} \bar{\xi}^- + S_{\alpha \beta} (f^n + f^C) \right] \right] \\
+ 6X(\bar{e}_{NC}, \bar{\gamma}_q) \bar{e}_{NC}^2 \left[ 4T n_{k_1} n_{k_2} n_{k_3} n_{k_4} n_{123} - \alpha_{123} \right] \right\} \\
C_{el}^{DE} = 16 \pi \gamma \sum_{k,k',k_1} G_{k,k',k_1}^2 D(k_1-k) \left\{ \bar{e}_k \bar{e}_k^{-1} X(\bar{e}_{k_1}, \bar{\gamma}_q) \left[ 4T N_{\bar{\rho}_\sigma} + k_B^{-1} (f^n + f^C) \right] \\
+ \bar{e}_{NC}^2 X(\bar{e}_{NC}, \bar{\gamma}_q) \left[ 4T n_{k_1} + k_B^{-1} \bar{e}_{k_1} (n_{k_1}^2 - 1) \right] \right\} \\
$$

It is observed from eqn. (12) that electron-phonon coupling coefficient ($g_k$) via $G_{k,k'}$ is present in all terms which depicts the importance of electron-phonon interaction in superconductivity phenomenon. The details of the symbol are described in references elsewhere [52-53].

5. Results and Discussion

In cubic anharmonicity the dependence of temperature and perturbed mode energy on the dominant term say $F_\alpha$ (Curley bracket terms of eqn. 12b) is shown in figure 1 which reveals that initially there is small effect of temperature on it up to the value of $\bar{\gamma}_q$ less than 2.0x10^{-14} (erg). As the temperature increases curve start increasing but the value of $F_\alpha$ becomes smaller at higher temperature for smaller value of $\bar{\gamma}_q$ as shown by figure (2) and figure 3.
It emerges from the present study that the general trends of the thermal and electrical properties of superconductors both in the normal and superconducting states can be successfully explained with the help of present formulation. The various trends of energy and temperature dependences exhibit the new features of the theory in addition to the automatic evolution of Cooper pair energies.

Acknowledgments
One of the authors Nitin P. Singh is thankful to Prof. B.D. Indu for his help in the theoretical calculation of EHC.

References
[1] Launay J de 1956 Solid State Physics (vol 2) eds. F Seitz and D Turnbull (New York: Academic Press) p 220
[2] Karlsson A V 1970 Phys. Rev. B 2 3332
[3] Hartmann W M, Culbert H V and Huebener R P 1970 Phys. Rev. B 1 1486
[4] Agrawal B K 1969 J. Phys. C 2 252
[5] Tiwari M D and Agrawal B K 1973 Phys. Rev. B 7 4665
[6] Tiwari M D, Kesharwani K M and Agrawal B K 1973 Phys. Rev. B 7 2378
[7] Indu B D, Tiwari M D and Agrawal B K 1978 J. Phys. F 8 755
[8] Pattalwar S M, Dixit R N, Shete S Y and Basu B K 1988 Phys. Rev. B 38 7067
[9] Urbach J S, Mitzi D B and Kapitulnik A 1989 Phys. Rev. B 39 12391
[10] Chakraborty A, Epstein A J and Cox D L 1989 Phys. Rev. B 39 12267
[11] Junod A 1990 Physical Properties of High Temperature Superconductors II, ed. D M Ginsberg (Singapore: World Scientific) p 13
[12] Atake T 1991 Thermochim. Acta 174 291
[13] Phillips N E, Fisher R A and Gordon J E 1992 Progress in Low Temperature Physics, (vol 13) ed D F Brewer (Amsterdam: North Holland) p 267
[14] Fisher R A, Gordon J E, and Phillips N E 1996 Annu. Rev. Phys. Chem. 47 283
[15] Greene LH and Bagley B G 1990 Physical Properties of High Temperature Superconductors II ed D M Ginsberg (Singapore: World Scientific) p 509
[16] Malozemoff A P 1989 Physical Properties of High Temperature Superconductors I ed D M Ginsberg (Singapore: World Scientific) p 71
[17] Wethamer N R 1970 Phys. Rev. B 1 572
[18] Ida Y 1970 Phys. Rev. B 1 2488
[19] Hui J C and Allen P B 1975 J. Phys. C 8 2923
[20] Zhdanov K R, Belosludov V and Rakhmankulov F S 1985 Phys. Stat. Sol. (b) 130 19
[21] Knapp G S, Bader S D, Culbert H V, Fradin F Y and Klippert T E 1975 Phys. Rev. B 11 4331
[22] Knapp G S, Bader S D and Fisk Z 1976 Phys. Rev. B 13 3783
[23] Indu B D 1992 Mod. Phys. Lett. B 6 1665.
[24] Buckingham M J 1951 Nature 168 281.
[25] Animalu A O E 1977 Intermediate Quantum Theory of Crystalline solids (Englewood: Prentice-Hall International).
[26] Eliashberg G M 1963 Sov. Phys. J. E. T. P. 16 780.
[27] Harrison W A 1970 Solid State Theory (New York: McGraw-Hill Inc)
[28] Allen P B and Hui J C K 1980 Z Physik B 37 33
[29] Labbe J and Bok J 1987 Europhys. Lett. 3 1225
[30] Labbe J 1989 Phys. Ser. T29 82
[31] Friedel J 1987 J. Phys. (Paris) 48, 1787; 49 1435
[32] Combescot R and Labbe J 1988 Phys. Rev. B 38 262
[33] Markiewic R S 1990 J. Phys. Cond. Matt. 2 665
[34] Markiewic R S and Giessen B C 1989 Physica C 160 497
[35] Tsuei C C, Newns D M, Chi C C, and Pattnaik P C 1990 Phys. Rev. Lett. 65 2724
[36] Newns D M, Tsuei C C, Pattnaik P C and Kanes C L 1992 Comments Cond. Matt. Phys. 15 273
[37] Indu B D 1990 Int. J. Mod. Phys. B 4 1379
[38] Painuli C P, Bhatt R M, Raiwani Y P, Srivastava S, Gairola S C, Gairola R P, Indu B D, and Tiwari M D 2004 Ind. J. Pure & Appl. Phys. 42 288
[39] Manheim P D 1968 Phys. Rev. 165 1011
[40] Agrawal B K 1980 Phys. Rev. B 22 6294
[41] Tiwari M D and Agrawal B K 1973 Phys. Stat. Sol. (b) 58 209
[42] Srivastava S, Raiwani Y P, Gairola S C and Indu B D 1996 Physica B 223 538
[43] Ghatak A K and Kothari L S 1971 An Introduction to Lattice Dynamics (London: Addison -Wesley Pub. Co.) p 94
[44] Barron THK 1963 Proc.of Int. Conf. on Lattice Dynamics(Copenhagen) p 301
[45] Harrison W A 1970 Solid State Theory (New York: Mc Graw-Hill Inc)
[46] Bahadur Rita and Sharma P K 1974 Solid State Commun. 15 621
[47] Zubarev D N 1960 Sov. Phys. Usp. 3 320
[48] Ashokan Vinod, Indu B D and Dimri A K 2011 AIP Adv. 1 032101
[49] Sharma P K and Bahadur Rita 1975 Phys. Rev. B 12 1522
[50] Ashokan V, Indu B D 2013 AIP Adv. 3 022108(1)
[51] Gupta A, Verma S K, Kumari A and Indu B D 2018 Int. J. Mod. Phys. B 32 1850237.
[52] Singh Anu, Singh Hempal and Indu B D 2016 AIP Adv. 6 075102-(1)
[53] Singh Anu and Indu B D 2018 AIP Conference Proceedings 1953 120036-(1)