Raman scattering in high temperature superconductors: An Integrated view

S. N. Behera*, Umesh A. Salian and Haranath Ghosh.
Institute of Physics, Bhubaneswar 751 005, Orissa, India.

Abstract

The common features in the Raman data of high temperature superconductors: (the cuprates, bismuthates, alkali doped fullerides and some organic superconductors), are analyzed. It was shown that qualitative understanding of the data can be achieved in terms of non-Fermi liquid models for their normal state, with appropriate bag mechanisms for the superconducting state.

Keywords: Non-Fermi Liquid theory, High temperature superconductors, Background Raman Intensity, Bag model of superconductivity.

I. INTRODUCTION

Over the years Raman scattering has proved to be a valuable tool for probing the normal as well as the superconducting (SC) states of the high temperature superconductors. It is well known that in the cuprate superconductors the measured Raman intensities have shown several unusual features [1], which are summarized elsewhere [2–4]. Similar behaviour of the Raman spectra has also been observed in other families of high temperature superconductors such as the bismuthates [5] the alkali doped fullerides [6] and the organic superconductors [7]. For example the Raman spectra of BKBO ($Ba_{0.6}K_{0.4}BiO_3$) in the metallic state shows two phonons out of which the lower frequency one develops an assymetric line shape and the other with higher frequency softens on lowering the temperature. Furthermore, a new peak appears below certain temperature which persists in the SC state. In contrast these features are not present in the insulating samples. On the other hand in case of alkali doped fullerenes and the organic superconductor ($BEDT-TTF)_2I_3$ the intensities of some of the phonons are suppressed in the metallic state or on going to the SC state respectively. Again in all these systems except for the alkali doped fullerenes a constant intensity background has been reported, which is attributed to scattering by charge carriers.

The observation of these global features in the Raman spectra of the different families of the high temperature superconductors is rather surprising. The fact that these systems exhibit entirely different structures and properties suggests that the
normal state and their superconductivity may have entirely different origin. For example the cuprates and the organic SC are two dimensional systems whereas the bismuthates and the alkali doped fullerides are three dimensional in nature. Similarly the cuprates exhibit antiferromagnetic order and are Mott insulators in their undoped state whereas the bismuthates are well known to be charge density wave (CDW) insulators \[8\]. There is some evidence (e.g. existence of nested pieces of Fermi surface) in favour of the CDW state being the ground state in the case of the other two systems as well \[9,10\], namely the alkali doped fullerides and the organic superconductors.

The other unexpected feature is the observation of the constant intensity background in the Raman spectra in almost all the high \(T_c\) systems, which was never observed before for a usual metal. The charge carrier scattering essentially involves the polarizability which for a Fermi liquid like metal is given by the Lindhard function. Since the inelastic light scattering takes place with no momentum transfer, the Lindhard function vanishes at \(q = 0\), hence there is no scattering by charge carriers in a metal. Again the phonon self energy in a usual metal will also vanish for the zone centre phonon, prohibiting any observable change in the phonon peak. The very fact that in the high \(T_c\) systems charge carrier scattering as well as phonon anomalies has been observed points to the fact that the normal states of all these systems exhibit non-Fermi liquid like behaviour. Furthermore, the unexpected frequency and temperature dependence of the imaginary part of the polarizability, deduced from the fact that the background intensity is constant even indicates that the normal state of all these systems is a marginal Fermi liquid \[11\].

Following this dictum we have proposed (i) a strongly correlated metallic state for the cuprates \[2,3\] and (ii) a fluctuating CDW state to be the ground state for the bismuthates, the alkali doped fullerides and the organic superconductor \((BEDT-TTF)_{2}I_3\). Both of these states have non-Fermi liquid excitation spectra, and a lot of other similar characteristics. Superconductivity in both these systems arises because of a bag mechanism \[2,3,8–10\]. In what follows we shall provide qualitative accounts of these models (Sec. 2) and calculate the Raman scattering intensity (Sec. 3). Some results of recent calculations are presented in Sec. 4 for the cuprates, bismuthates and alkali doped fullerides, which are obtained by adopting these models to the respective systems.

II. NON-FERMI LIQUID NORMAL STATES AND SUPERCONDUCTIVITY

The phase diagrams of the cuprates are dominated by an antiferromagnetic ground state for the undoped system which is a consequence of strong electron correlation. On doping with charge car-
riers the system becomes a Mott insulator with short range magnetic correlations. This state is proposed to be a resonating valence bond (RVB) insulator [12], which on further doping undergoes an insulator-metal transition. Doping charge carriers, while turning the RVB insulator into a metal also creates strong fluctuations in the RVB state, which corresponds to the spontaneous breaking and making of these bonds. The quanta of these fluctuations which are the collective modes of the RVB state, therefore interact strongly with its elementary excitations. This interaction in fact is the most crucial ingredient of the strongly correlated metallic state. The details of the correlated metallic state and its consequence on Raman scattering are presented in [2,3]. It was shown that this correlated metallic state exhibits marginal Fermi liquid behaviour. The effect of the strong interaction between the elementary excitations and the quanta of the collective modes of the RVB state is taken into account phenomenologically by assuming that as a consequence of this interaction the RVB gap becomes a pseudo gap existing only in some regions of the Fermi surface, leaving the Fermi surface intact in other regions, as was originally suggested by Bilbro and McMillan [13] for low dimensional systems.

With increasing dopant concentration, the region in the Fermi surface with the RVB gap shrinks. Ultimately when the gapped region of the Fermi surface vanishes, which can happen when the dopant concentration exceeds a critical value, there are no more bonds left in the metallic state and the normal state admits the usual Fermi liquid description and becomes a good metal. However it is only in the correlated (bad) metallic state that superconductivity appears [4]. This provides a good description of a large number of observed properties of the cuprates in the normal state.

The bismuthate (BaBiO$_3$) in its undoped form is known to be a CDW insulator, hence a description almost similar to the cuprates holds for the doped systems. On doping the system with impurities like K, holes are created in the fully occupied lower CDW band. On increasing the hole concentration the CDW gap will turn into a pseudo gap due to partial removal of nested pieces of Fermi surface. Furthermore creation of holes will cause strong fluctuation in the CDW order parameter, the quanta of these being the collective modes. These collective modes in turn will interact strongly with the elementary excitations of the CDW state. This interaction will dominate the normal state of the system, and when the dopant concentration exceeds a critical value the nesting of the Fermi surface is totally destroyed so the system falls back to the usual Fermi liquid like metal. Again superconductivity appears only in the nested metallic state. Thus the normal states of both the cuprates and the bismuthates are very similar in nature and their elementary excitations exhibit marginal Fermi liq-
uid behaviour, even though it is entirely of different origin in the two systems. This explains why the Raman spectra in the two systems exhibit similar features.

Superconductivity in these systems arises because of the pairing of the corresponding elementary excitations due to a bag mechanism \[14,8\]. In either case the elementary excitations are strongly interacting with the collective modes of the system. Therefore, there can be a collective mode mediated attraction between the elementary excitations which will give rise to pairing. In the original bag models \[14,8\] only the pairing of the holes in the lower band was considered. However in the present case since there exists only a pseudogap in these system there can be pairing of elementary excitations belonging to both the valence and conduction bands (lower and upper bands). This is the modified charge/correlation bag model for SC in the bismuthates/cuprates, which explains the experimental Raman data much better \[3,10\] as will be discussed below.

The fluctuating CDW metallic state and the modified charge bag model can also be adopted to the alkali doped fullerides \[9\] and the organic superconductors \[10\].

### III. RESULTS FOR RAMAN INTENSITIES

The total Raman intensity in general is proportional to \[I\].

\[
I(q, \omega) = [1 + n(\omega)][\sum_i (-Im\chi_i(q, \omega)) + \sum_j [ImD_j(q, \omega)]]
\]

where \(\chi_i(q, \omega)\) are the wave vector (q) and frequency (\(\omega\)) dependent polarizabilities, \(D_j(q, \omega)\) are the Green’s functions of the various Raman active phonons and \(n(\omega)\) is the Bose factor. It should be noted that the same polarizability functions which determine the charge carrier scattering also provide the self energy to the phonons. The polarizability functions have to be calculated for the normal and the SC states in order to determine the Raman intensities. As described earlier \[3,10,15\] in these systems there exist two different kinds of phonons which contribute to Raman scattering, (i) the usual zone centre (\(q=0\)) optic phonons (the propagating ones) and (ii) the zone folded (\(q=Q\)) phonons which arise due to the superperiodicity of the antiferromagnetic (CDW) order in the cuprates (bismuthates). Since in the doped systems the long range order is reduced to a local order, the later category of phonons will be more localized in nature. These two intereact differently with the charge carriers, while the propagating ones couple to the charge carrier density (the usual electron-phonon interaction) the localized ones interact with
the collective (amplitude) modes of the RVB/CDW condensate in the normal state. In calculating the polarizability the density of states at the Fermi level is divided into two parts $N(0) = N_1(0) + N_2(0)$, where $N_1(0)$ corresponds to the region of the Fermi surface with a gap in the normal state and $N_2(0)$ to the region where the gap vanishes. This is how the Bilbro-McMallian approximation is implemented. With this prescription the Raman intensities are calculated.

In the case of the cuprates the results of a zero temperature calculation for $q=0$, was presented in [2], while that of a finite temperature calculation for the correlated metallic state as well as the correlation bag model of superconductivity was reported in [3]. The finite temperature study involved a low and high temperature expansion of the Fermi functions [3]. Furthermore a small $q$, but zero temperature calculation was carried out to account for the penetration of the electromagnetic radiation into the sample (the skin depth). The cuprates being bad metals (extreme type II materials) in their normal (SC) states the skin depths are rather large which justifies the small $q$ expansion. The calculated Raman intensities within this approximation was presented in [4] which shows qualitative agreement with the Raman data. The finite $q$ calculation also yields the phonon dispersion which is plotted in Fig.1(a) for the propagating mode. The figure shows the dispersion in the normal and the SC states [14]. The merger of two phonon branches in the normal state and the splitting of a branch into two branches in the SC state are noteworthy. Correspondingly the peaks in the spectral density function approach each other and merge(split) into one(two) peak beyond (below) a certain wave vector.

In the SC state the lowest frequency branch has very little intensity as seen from the plot of the spectral density functions. Therefore the difference in the phonon frequencies of the lower branch of the normal state and the branch appearing just below it in the SC state was taken to be the wave vector dependent shift. Figure 1(b) shows this wave vector dependent softening of the phonon frequency of the lower branch on going over to the superconducting state. Note that the shift in phonon frequency with wave vector increases at first and then saturates. This is in qualitative agreement with the results of neutron scattering measurements [17]. The Raman intensity calculations for the cuprates was discussed at length in [2–4,15].

In the bismuthates the fluctuating CDW state and the modified charge bag model [18] provide a good description of the normal and the SC states respectively.

Fig 2(a). Calculated Raman intensity at three different temperatures using the temperature expansion approximation.
In the K-doped system two phonons have been observed \[5\]. The high frequency one is taken to be the propagating and the low frequency one to be the localized phonon. The CDW gap lies between the two phonons. The Raman intensities are calculated at finite temperatures by two different methods (i) by making high and low temperature expansions, and (ii) by performing an all temperature calculation, both of which are carried out numerically. The temperature expansion results for the normal state are shown in Fig.(2a) for three different temperatures. It can be seen that in this approximation the low frequency phonon looses its intensity drastically, while it hardens and broadens as the temperature is lowered (increasing $c_1$). The high frequency phonon as well as the constant background intensity are not effected very much with decreasing temperature. In the improved calculation (for all temperature) the results of which are depicted in Fig.(2b), the supression of the low frequency phonon is reduced considerably.

Fig 3. Variation of the Raman intensity with dopant concentration

The adoption of the model involving the fluctuating CDW state and the charge bag superconductivity to the alkali doped fullerides requires a careful analysis of the Raman data \[19\]. In this system the Raman spectrum shows several (at least 10) phonon peaks in the case of the insulating solid fullerite. Most of these phonons arise from the intramolecular vibrations of the carbon atoms in $C_{60}$. Two of these phonons are of $A_g$ symmetry and the rest with decreasing temperature. Experimental measurements have shown that on lowering the temperature the low frequency phonon acquires a shift and a Fano-line shape, while a new peak emerges in between the two peaks. The later can be identified with the kink corresponding to the CDW gap. Furthermore the results of the temperature expansion calculation has an unphysical divergence of intensity at zero frequency, which is rectified in the all temperature calculation as shown in Fig.(2b).
all have $H_g$ symmetry. On going over to the alkali doped fulleride $A_3C_{60}$ ($A = K, Rb$) the system becomes a metal and Raman intensity of most of the $H_g$ modes is suppressed. Which again reappears in the insulating $A_6C_{60}$ samples. The suppression of the intensity is attributed to the strong coupling of these phonons to the doped charge carriers, because of which the phonons acquire a large width. Since the intramolecular modes are effected, in our interpretation these should be the zone folded phonons. Therefore the CDW state is intramolecular in nature corresponding to the transition from a uniform bond length between the carbon atoms to the stable structure of long and short bonds of the fullerene molecule. Under this assumption the CDW gap will correspond to the band gap which is rather large ($\sim 1$ ev). Since the Raman continuum appears only above the CDW gap, it will not be observable in the Raman spectrum, at least in the frequency region where the phonons are there. This is clearly depicted in Fig. 4, which also shows the temperature dependence of the Raman spectrum in the metallic (doped) state. Note the relative suppression of the intensities of three of the phonons compared to those in the insulating state (not shown in figure). In the latter state all the phonons will have the same intensity as there is no self energy for them. It is also clear from the figure that on lowering the temperature (increasing the parameter $c_1$) the intensity of some of the phonons is suppressed considerably. Furthermore, the suppressed phonons show a hardening of their frequency and undergo substantial broadening. All these features are in agreement with the experimental observations. A particular success of the model is that it provides an explanation as to why a Raman continuum has not been observed in alkali doped fullerenes. The variation of Raman intensity with change in the dopant concentration and the coupling constant has also been studied and will be reported elsewhere [19].

In the above modeling of the fluctuating CDW state for the alkali doped fullerenes, it is unlikely that the large CDW gap will ever vanish with doping.

Fig 4. Raman intensity for the alkali doped fullerenes.

Hence superconductivity in this system will arise only due to the pairing of quasiparticles in the upper band as proposed in the original charge bag model [8]. In this model the calculated Raman intensity [20] in the SC state does not show much change from that in the normal state. Again this is in agreement with the experimental observations for the alkali doped fullerenes.

Similar adoption of the model to the organic superconductor $(BEDT - TTF)_2I_3$ has been reported earlier [14]. This organic SC being a 2D-system, the fluctuating CDW state and the charge bag model has been adopted to it. A zero temperature calculation of the Raman intensity [13] has
qualitatively reproduced the experimental observations.

In conclusion it was shown that most of the features observed in the Raman data can be understood in terms of the proposed non-Fermi liquid descriptions of the normal states of these systems and the corresponding bag mechanism for superconductivity.

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REFERENCES

[1] S. L. Cooper and M. V. Klein, Comments Condens. Mat. Phys. 15 (1990) 99

[2] Debanand Sa and S. N. Behera, Physica C 203 (1992) 347

[3] Debanand Sa and S. N. Behera, Physica C 226 (1994) 85

[4] S. N. Behera and Umesh A. Salian, Solid State Comm. 91 (1994) 354

[5] K. F. McCarty, H. B. Radousky, D. G. Hinks, Y. Zheng, A. W. Mitchell, T. J. Folkerts and R. N. Shelton, Phys. Rev. B 40 (1989) 2662

[6] S. J. Duclos, R. C. Haddon, S. Glarum, A. F. Hebard and K. B. Lyons, Science 254 (1991) 1625

[7] K. L. Pokhodnia, A. Graja, M. Weger and D. Schweitzer, Z. Phys. B 90 (1993) 275

[8] D. M. Gaitonde and S. N. Behera, Physica C 173 (1991) 293 and references therein

[9] S. N. Behera and Haranath Ghosh in “Clusters and Nanostructured Materials” Eds. P. Jena and S. N. Behera (Proceedings of the Puri Workshop) (Nova Science Publishers Inc. N.Y. (1995)) to appear.

[10] S. N. Behera and Haranath Ghosh, Z. Phys. B 95 (1994) 275 and references therein; Haranath
Ghosh and S. N. Behera, Ind. Jr. Phys 69 A (1995) 14.

[11] C. M. Verma, P. B. Littlewood, S. Schmitt-Rink, E. Abrahams and A. E. Ruckenstein, Phy. Rev. Lett. 63 (1989) 1996

[12] G. Baskaran, Z. Zou and P. W. Anderson, Solid State Comm. 63 (1987) 973

[13] G. Bilbro and W. L. McMillan, Phys. Rev. B 14 (1976) 1887

[14] J. R. Schreiffer, X. G. Wen and S. C. Zhang, Phys. Rev. Lett. 60 (1988) 944 and Phys. Rev. B 39 (1989) 11663

[15] S. N. Behera, P. Entel and D. Sa in Proceedings of the “International Symposium on Local Order in Condensed Matter Physics”, Eds. P. Jena and S. D. Mohanty, (Nova Science Publishers 1995).

[16] Haranath Ghosh, Physics Teacher 36 (No. 3 - 4) (1995) 71.

[17] Umesh A. Salian and S. N. Behera, Unpublished calculations.

[18] N. Pyka, W. Reichardt, L. Pintschovius, G. Engel, J. Rossat-Mignod and J. Y. Henry, Phys. Rev. Lett. 70 (1993) 1457.

[19] Haranath Ghosh and S. N. Behera, Unpublished calculations.

[20] D. M. Gaitonde, Ph.D thesis (unpublished).