Title:

Electronic Raman Scattering in High-T_c Superconductors

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1 Introduction

Raman spectroscopy is widely used in the investigation of elementary excitations in solids. Its has been applied extensively to phonons, excitons, magnons, spin fluctuations, spin waves in bulk and superlattice semiconductors and metals (Cardona and Güntherodt, 1983-2000). Electronic excitations have become of much interest in the investigation of superconductors, in particular after the discovery of high-T_c superconductors with transition temperatures in excess of 100 K. The contribution of electrons to the Raman signal, which will be discussed in this article, gives information about the excitations at the Fermi surface and hence about the pairing mechanism, which is difficult to obtain otherwise. A particular issue in the high-T_c superconductors, the symmetry of the superconducting gap $2\mathbf{\Delta_k}$ in the CuO_2-based materials has been central to much of the research. A *d*-wave-like gap finds most support from experi-

ment, i.e., the gap function may be described by $\mathbf{\Delta_k}(\phi) = \Delta_0 \cos(2\phi)$, where $\phi = 0$ corresponds to a direction along a Cu-O bond in the CuO_2 plane. Scattering by phonons and magnons, on the other hand, has lead to a detailed understanding of the vibrational and magnetic properties of the high-T_c materials (Thomsen, 1991) and, through electron-phonon coupling, to estimates of the magnitude of the superconductivity-related gap, but not its symmetry (Thomsen and Kaczmarczyk, 1998); these will not be subject of this article.

Groundlaying work on the theory of Raman scattering was performed by Abrikosov and Fal'kovskiĭ (1961), Abrikosov and Genkin (1974), and, together with experiments on V_3Si, a superconductor with a T_c of $17\,K$ and an isotropic s-wave like gap, by Klein and Dierker (1984).

2 Experimental

The electronic Raman signal in the nearly tetragonal high-T_c superconductors is weak in structure; above the transition temperature T_c of the superconductor it is completely flat in all scattering geometries (with different amplitudes) and extends to large Raman shifts ($\geq$ 1eV). In the one-phonon region the signal is superimposed by the sharp Lorentz peaks from the lattice vibrations. Below T_c, in the $T \rightarrow 0\,\mathrm{K}$ limit, the signals rise from zero either linearly with frequency (A_{1g} or B_{2g}), with a cubic frequency term (B_{1g}), or both, depending on the scattering geometry and on the type of distortion of the crystal from tetragonal symmetry. The signal has a maximum at an energy

related to the magnitude of the energy gap $2\Delta_0$ of the superconductor. At large frequencies ($\omega/k_BT \gg 1$) the signal remains flat and unaffected by temperature. The first results on $YBa_2Cu_3O_7$ were reported soon after its discovery (Lyons et al., 1987; Ossipyan et al., 1988; Thomsen et al., 1988), and among other things, have lead to the prediction that high-T_c materials may be described as "marginal" Fermi liquids (Varma et al., 1989).

Raman scattering is sensitive to the superconductivity-related gap symmetry through the selection rules and through the energy dependence of the scattering amplitude at low energies ($\hbar\omega/2\Delta_0 \leq 1$) (Devereaux et al., 1994; Strohm and Cardona, 1997; Wu and Carbotte, 1998; Misochko, 2000). In addition, the absolute experimental scattering efficiencies may be compared with predictions of theoretical approaches (Strohm and Cardona, 1997). Figure 1 shows the Raman spectra of $YBa_2Cu_3O_7$ for 5 different scattering geometries (upper panel) and the corresponding 3 different Raman symmetries (lower panel), which were extracted from the spectra according to $A_{1g} = (I_{xx} + I_{yy})/2 - I_{x'y'}$, $B_{1g} = I_{x'y'} - I_{xy}$ and $B_{2g} = I_{xy}$. The phonons have been removed numerically from the data. Other high-T_c superconductors show similar features (although with different amplitudes), and the spectra in Fig. 1 are representative of electronic Raman scattering in these materials.

3 Theory

Electron scattering in the free-particle picture cannot lead to the observed scattering. The screening by the electron gas introduces a factor $|\varepsilon(q,\omega)|^{-2}$ into the scattering cross section [$\varepsilon(q,\omega)-$dielectric function of the electron gas] and, far below the plasma frequency, strongly screens the single-electron scattering (Klein, 1983). A larger contribution comes when invoking band structure effects in solids. The efficiency for (Stokes) Raman scattering, in the absence of resonances, may be described in terms of the effective-mass tensor $m^\star$ by

$$\frac{d^2\sigma}{d\omega d\Omega} \sim \left(\mathbf{e}_L \frac{1}{m^\star} \mathbf{e}_S\right)^2 q^2 \left[n(\omega)+1\right] \mathrm{Im}[\varepsilon^{-1}(q,\omega)] \qquad (1)$$

where $\mathbf{e}_{L,S}$ are the electric-field vectors of incident and scattered light, respectively, q is the momentum of the emitted phonon, and $n(\omega) = [\exp(\hbar\omega/k_BT)-1]$ is the Bose factor. The scattering as described by Eqn. (1) for a single, possibly anisotropic carrier type, is screened as well due to the small momentum transferred in light-scattering experiments ($q = \pi/\lambda$ in backscattering geometry, typically $q \approx 0.5\ 10^{-5}$ cm^{-1}). In multivalley systems, however, there may be effective-mass fluctuations around the Fermi surface *without* charge fluctuations, a phenomenon known from multivalley semiconductors like Si or Ge (Abstreiter et al., 1984), leading to unscreened scattering *via* Eqn. (1).

The absolute square of the gap function $\mathbf{\Delta_k}$ enters the scattering efficiency through the Raman susceptibility, which, in the random phase approximation, may be written as the sum of an unscreened and a screening part (Strohm and Cardona, 1997). The screening part vanishes for non-fully symmetric scattering, i.e., in exactly tetragonal systems only A_{1g} symmetry is screened. It is important to note that because of the absolute square of $\mathbf{\Delta_k}$ entering the Raman susceptibility, the sign of the gap function cannot be determined. An anisotropic gap of s-wave symmetry with small minima in the four $\pi/4$-directions (say $\Delta_0|\cos(2\phi)| + \Delta_{\rm min}$ and $\Delta_{\rm min}/\Delta_0 \ll 1$) could not be distinguished from "true", i.e. sign changing, d-wave symmetry in this approximation of the theory. Scattering of electrons by impurities can make this distinction possible (Devereaux, 1995).

It is possible to evaluate Eqn. (1) for the specific bandstructures of the high-T_c superconductors and obtain symmetry, functional dependence on ω at low energies, and absolute magnitude of the scattering efficiency. Within the validity of the bandstructure calculation and within the order perturbation theory of the effectiv-mass approximation this approach is exact. The result of a 3 dimensional Brillouin zone integration over the bandstructure of $YBa_2Cu_3O_7$ obtained in the local-density approximation is shown in Fig. 2. Three curves are given, the unscreened scattering efficiency, the screening contribution and the total scattering in absolute magnitude in terms of the frequency ω normalized to Δ_0. It is seen, that the A_{1g} and B_{1g} contributions peak at $2\Delta_0$

and, in particular, that screening does not affect the position of the A_{1g}-peak, a still unresolved point of controversy in the literature. In the experiment in Fig. 1 A_{1g} and B_{1g} symmetries peak at energies differing by about a factor of two, which has been ascribed to screening effects in A_{1g} symmetry (Devereaux et al., 1994). Given that this is apparently not the case, the value of the gap maximum in the A_{1g} spectra is in accordance with experiments on the phonon self-energies, which predict a similar value for $2\Delta_0$ (Friedl et al., 1990). A possible reason for the shift of the B_{1g} maximum to higher energies is a gap function with a symmetry more complicated than strict d-wave.

The absolute amplitudes of calculated and measured electronic Raman signal come out in good agreement for the various scattering geometries, giving confidence to the theoretical approach. As the experimental scattering efficiency is difficult to deterimine better than to a factor of 2, the remaining deviations can be considered small. Also, the experimental values are usually smaller than the calculated ones, which do not include any resonance contribution.

The frequency dependence at low energies is seen to be explained correctly by the calculation as well. While the A_{1g} component is linear at low energies as expected for a d-wave gap in an idealised, strictly tetragonal crystal structure, the B_{1g} component should be cubic (Devereaux et al., 1994). This is because a $d_{x^2-y^2}$ gap has modes along $x+y$ and $x-y$ directions and thus a linear contribution to the density of states for A_{1g} scattering. The B_{1g} Raman vertex, however, vanishes for the same directions, giving rise to an overall ω^3

dependence at low energies. The real crystal structure in most high-T_c superconductors is slightly distorted into orthorhombic symmetry; this can occur in two different ways (Fig. 3). In $YBa_2Cu_3O_7$ the B_{1g} component becomes fully symmetric (A_g in D_{2h}) and acquires a linear component in the low-energy scattering at low temperatures. The ratio of the linear to cubic components at $\omega = 300$ cm^{-1} is about 1 from experiment and agrees reasonably well with 0.35 from the calculation (Strohm and Cardona, 1997). The calculated value is enhanced further when impurity scattering is included. In $Bi_2Sr_2CaCu_2O_{8+\delta}$, on the other hand, due to the rotated distortion, the scattering remains of B_{1g} symmetry and continues to coincide with the gap function. It is expected to have a much smaller or vanishing linear contribution, a result which is found in the $Bi_2Sr_2CaCu_2O_{8+\delta}$ spectra of (Staufer et al., 1992), where the ratio of the linear to cubic term is 0.07.

4 Conclusion

Electronic Raman scattering is largely consistent with a d-wave-symmetry gap in high-T_c superconductors. The low-energy dependence and the absolute magnitude of the scattering signal of $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$ are in agreement with a non-resonant, 3 dimensional effective-mass approximation calculation. Screening does not affect the relative positions of A_{1g} and B_{1g} peaks noticeably; the magnitude of the gap can best be identified with the maximum in A_{1g} scattering geometry. The reason for the experimentally

observed shift of the B_{1g} peak to higher energies remains to be understood.

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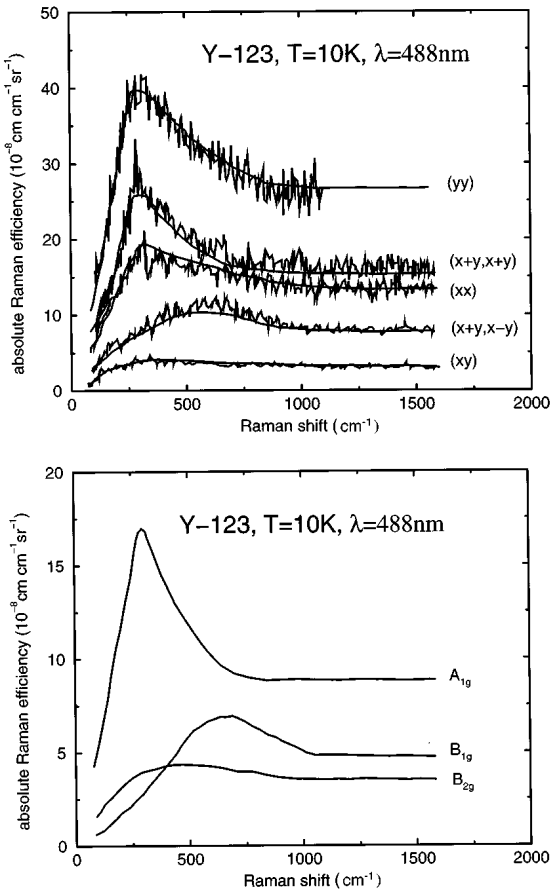

Fig. 1. Electronic Raman spectra of $YBa_2Cu_3O_7$ at 10K excited at a laser wavelength of $\lambda = 488$ nm. The labels refer to polarisations of incident and scattered light with respect to the crystal axis (upper panel) and to the symmetry of the excitation in tetragonal notation (lower). From (Strohm and Cardona, 1997).

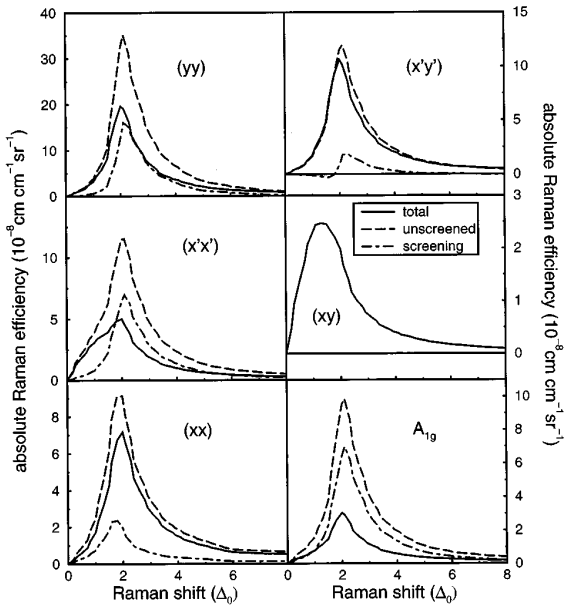

Fig. 2. Calculated Raman spectra of $YBa_2Cu_3O_7$ for different scattering geometries (left panels) and symmetries (right). Note the different scales on the ordinate. From (Strohm and Cardona, 1997).

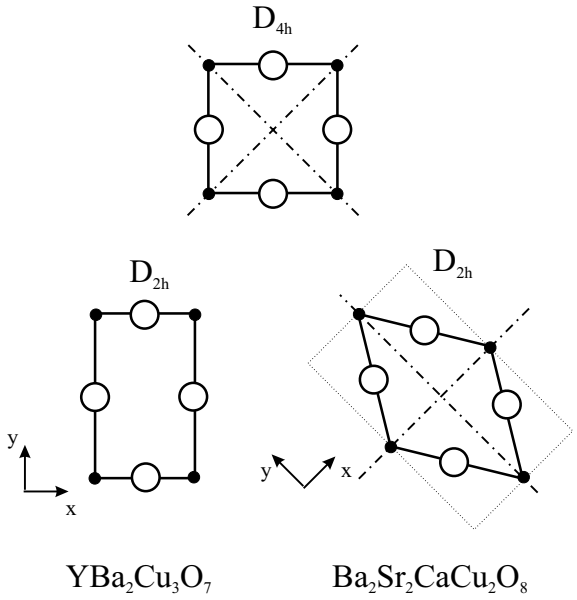

Fig. 3. Two different ways of distorting tetragonal (D_{4h}) to orthorhombic (D_{2h}) symmetry. They occur, e.g., in $YBa_2Cu_3O_7$ (left) and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (right). Note that the diagonal mirror planes of the CuO_2 square are lost in one case only. Closed symbols represent Cu atoms, open ones O atoms in the CuO_2 plane of high-T_c superconductors. The distortion is vastly exaggurated to clarify the point, in reality it is $(b-a)/b \approx 2\%$ in $YBa_2Cu_3O_7$ and $\approx 0.2\%$ in $Bi_2Sr_2CaCu_2O_{8+\delta}$.