Coupling of Phonons to Crystal-Field Excitations in $NdBa_2Cu_3O_{7-\delta}$

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We demonstrate the existence of a coupled elementary excitation involving a phonon and a Nd^{3+} $4f$-electron crystal-field excitation in the high-T_c superconductor $NdBa_2Cu_3O_{7-\delta}$. It explains in a natural way the recent observation of a double-peak structure in the Raman spectra as well as in the inelastic neutron scattering spectra near 300 cm^{-1} at low temperature. Our assignment is supported by measurements of the dependence of this feature on temperature, isotopic substitution, and polarization. A model based on strong coupling of extended phonon states to localized crystal-field excitations describes the observed behavior well.

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Recent measurements of the Raman scattering[1] as well as inelastic neutron scattering spectra[2] of $NdBa_2Cu_3O_y$ showed at low temperatures a double-peak feature near 300 cm^{-1} where only one peak is expected.

For all other 1:2:3 materials one observes in the Raman spectra in this frequency range only one phonon line, corresponding to the out-of-phase motion of the plane oxygen atoms [O(2) and O(3)].[3] Yoshida *et al.* argue[1] that the double peak in $NdBa_2Cu_3O_y$ corresponds to in-phase as well as out-of-phase motion of O(2) and O(3). They attribute another peak near 430 cm^{-1} to the x- (y-) directed B_{2g} (B_{3g}) motion of the apical oxygen [O(4)], although this feature is usually assigned[3] to the O(2) and O(3) in-phase motion.

Allenspach *et al.* (Fig. 1 of Ref. 2) also observed in the same material a very similar double peak (attributed to "distorted crystal-field excitations" due to oxygen vacancies) in their inelastic neutron scattering spectra whose intensity originates from scattering by crystal-field (CF) excitations within the Nd^{3+} $4f$-electron configuration, although only one such CF excitation is expected[4] in this energy range.

In this Letter, we first describe our Raman scattering spectra of $NdBa_2Cu_3O_{7-\delta}$ and their dependence on oxygen isotope, temperature, and polarization, and point out why the assignment of Yoshida *et al.* cannot be correct. We explain the 300-cm^{-1} doublet mentioned above by assuming a strong coupling (and thus also mixing) of the O(2) and O(3) out-of-phase phonon with a CF excitation of a slightly lower frequency. In particular, a surprising experimentally observed dependence on isotopic substitution and temperature follows from our model. After an introduction to the CF properties of the $4f$-electron states in $NdBa_2Cu_3O_{7-\delta}$, we calculate the Raman spectra for a coupled phonon–CF-excitation system, and show that we can explain our observations within this picture. A similar effect has been reported[5] and interpreted[6,7] previously for the Laves-phase material $CeAl_2$. Our model extends that of Thalmeier and Fulde[6,7] in that it also includes higher phonon quantum numbers.

We grew $NdBa_2Cu_3O_7$ single crystals using K_2CO_3 as a flux.[8] The ceramic $NdBa_2Cu_3{}^{16}O_7$ samples were prepared by standard methods. T_c was 95 K according to susceptibility measurements. The oxygen content was determined to be $O_{7.0}$ by a chemical analysis. Two of the ceramic samples were annealed for 115 h at 600 °C in an ^{18}O atmosphere so that 86% of the ^{16}O was indeed replaced (thermogravimetric analysis) by ^{18}O. We will mostly focus on the ceramic samples in order to compare the ^{16}O and ^{18}O data.

The Raman spectra were excited with the 5145-Å line of an Ar^+ laser and recorded with an ITT MEPSICRON multichannel system. The polarized spectra of the $NdBa_2Cu_3O_7$ single crystal measured at 10 K are shown in Fig. 1. We use the Porto notation $i(jk)l$ for

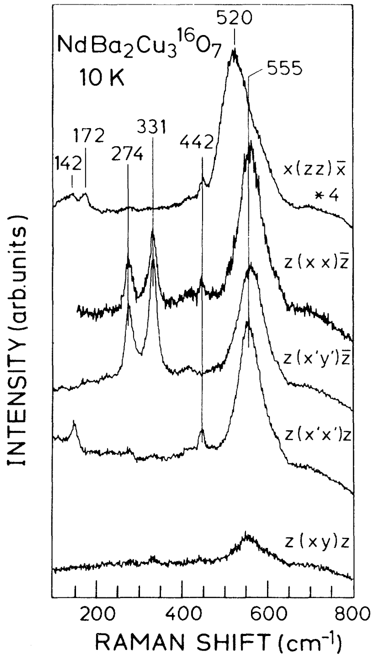

FIG. 1. Polarized Raman spectra at 10 K of a $NdBa_2Cu_3{}^{16}O_7$ single crystal.

the polarization geometry, where i and l denote the direction and j and k the polarization of incident and scattered light, respectively. x' and y' are rotated by 45° with respect to x and y around the z axis. Three peaks at 142, 172, and 442 cm^{-1} are observed in $z(xx)\bar{z}$ and $z(x'x')\bar{z}$ but not in $z(x'y')\bar{z}$ and $z(xy)\bar{z}$ geometry, whereas both peaks of the structure near 300 cm^{-1} (which are the main subject of this paper) are detected in $z(xx)\bar{z}$ and $z(x'y')\bar{z}$ but not in $z(x'x')\bar{z}$ and $z(xy)\bar{z}$ configuration.

Since the environment of rare-earth atoms and the CuO_2 planes is nearly tetragonal, we will mostly describe the symmetries of elementary excitations by representations of the tetragonal group D_{4h} ($4/mmm$). The six peaks have different symmetries in the D_{4h} group: B_{1g} for the peaks at 274 and 331 cm^{-1} and A_{1g} for the three others. The 274-cm^{-1} mode hence cannot correspond to O(2) and O(3) in-phase motion (as suggested by Yoshida *et al.*) since it does not have A_{1g} but rather B_{1g} symmetry. A more detailed discussion of these spectra (also of the unexpected polarization dependence of the 520, 555-cm^{-1} peak) will be published elsewhere.[9]

Figure 2, left panel, shows the dependence of the double-peak structure on temperature in the $NdBa_2Cu_3O_7$ ceramic sample. When the temperature is lowered, the upper mode shifts to higher frequencies by 17 cm^{-1}, while a bump at its *low*-frequency side increases in intensity and shifts to lower frequencies and finally becomes a strong peak. At room temperature the feature is asymmetric and very broad [much broader than in the conventionally behaving $YBa_2Cu_3O_7$ (Ref. 10)], and it even seems to exhibit some substructure. (For the single crystal of the same composition the overall behavior is similar.[9])

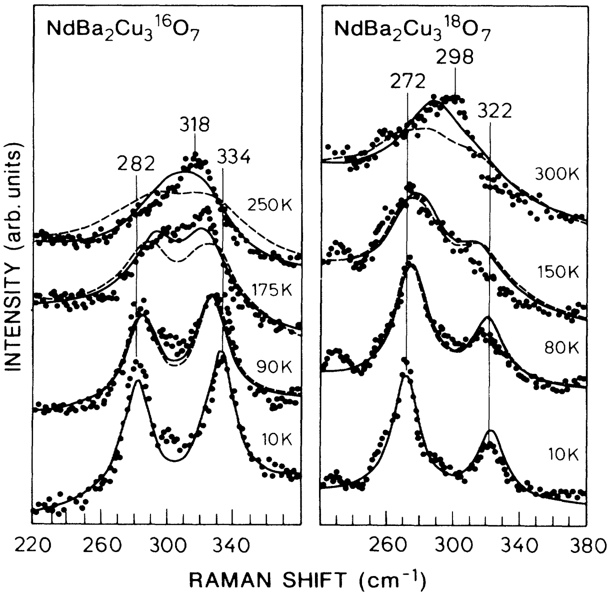

FIG. 2. Temperature dependence of the Raman spectra of $NdBa_2Cu_3{}^{16}O_7$ (left panel) and $NdBa_2Cu_3{}^{18}O_7$ (right panel) ceramic samples. The dots are the experimental data while the solid and dashed curves represent a fit with Eq. (3) with and without anharmonic contributions, respectively. The parameters are $\omega_{\mathrm{ph}}({}^{16}\mathrm{O})=308\ \mathrm{cm}^{-1}$, $\omega_{\mathrm{ph}}({}^{18}\mathrm{O})=\sqrt{16/18}\,\omega_{\mathrm{ph}}({}^{16}\mathrm{O})=290\ \mathrm{cm}^{-1}$, $\omega_{\mathrm{CF}}=304\ \mathrm{cm}^{-1}$, $V=37\ \mathrm{cm}^{-1}$, and $\kappa=2.6\times10^{-3}\ \mathrm{K}^{-1}$ (^{16}O) or $2.1\times10^{-3}\ \mathrm{K}^{-1}$ (^{18}O).

In the case of $NdBa_2Cu_3{}^{18}O_7$, however, the temperature dependence is very different (Fig. 2, right panel): When cooling down from 300 K, a peak grows on the *high*-frequency side. The splitting of the peaks at 10 K is similar to the case of ^{16}O. The isotopic shift at 300 K is $\approx 20\ \mathrm{cm}^{-1}$, i.e., 6.3%; at 10 K, both peaks shift by only $\approx 11\ \mathrm{cm}^{-1}$, i.e., 3.4% as compared to 6.0% expected for a one-phonon excitation and complete isotopic substitution.

The experiments can be summarized as follows: (i) We observe a double peak whose components both have clear B_{1g} (D_{4h}) symmetry. (ii) The splitting increases with decreasing temperature. (iii) At 300 K the lower peak vanishes for ^{16}O samples while the upper one does so for ^{18}O-substituted samples. (iv) The isotopic shift depends on temperature.

Before we proceed with the explanation of these results we briefly describe the influence of the CF on the Nd^{3+} f electrons and discuss the symmetry of the expected CF excitations.

The ground state of the three $4f$ electrons in Nd^{3+} is ${}^4I_{9/2}$, i.e., tenfold degenerate. If the ion is inserted in a tetragonal (D_{4h}) environment, the Nd^{3+} ground state splits into three M_6^- and two M_7^- doublets (notation of Ref. 11). All states have odd parity due to the odd number of $4f$ electrons. If the symmetry is further lowered to orthorhombic D_{2h}, no additional splitting can occur according to the Kramers rule;[12] now all states have M_6^- symmetry (D_{2h}). Exactly one linear combination of the degenerate basis states is occupied in each unit cell. Boltzmann statistics governs the occupation of those levels.

Excitations between two possible $4f$ states $|i\rangle$ and $|j\rangle$ can be treated as quasiparticles in a solid containing the rare-earth atoms. Their symmetry is the direct product of the representation of $|i\rangle$ and $|j\rangle$. We obtain (D_{4h})

$$\begin{aligned} M_6^- \times M_6^- &= M_7^- \times M_7^- = A_{1g}+A_{2g}+E_g\,, \\ M_6^- \times M_7^- &= M_7^- \times M_6^- = B_{1g}+B_{2g}+E_g\,. \end{aligned} \tag{1}$$

These excitations are Raman active if they transform like a second-rank tensor (D_{4h} point group—A_{1g}: x^2+y^2, z^2; B_{1g}: x^2-y^2; B_{2g}: xy; E_g: xz, yz). They can also be measured by inelastic neutron scattering provided they transform like the components of an angular momentum operator J (D_{4h}—A_{2g}: J_z; E_g: J_x, J_y). This has been done by Goodman, Loong, and Soderholm[4] who found CF-split levels at 0, 97, 168, 290, and 944 cm^{-1}. One can deduce[9] from Ref. 4 that in the tetragonal approximation the first and fourth doublets have M_6^- and M_7^- (D_{4h}) symmetry so that the CF excitation at 290 cm^{-1} between these two levels has $B_{1g}+B_{2g}+E_g$ symmetry.

If two elementary excitations have the same symmetry, they can couple. This leads to a renormalization of the frequencies and eigenvectors depending on the coupling strength. The rare-earth CF excitations should interact significantly with the phonons of the plane oxygen (since they distort strongly the CF around the Nd^{3+} ions) if both have a similar energy. For $\text{NdBa}_2\text{Cu}_3\text{O}_7$, this is the case for the B_{1g} CF excitation and the B_{1g} phonon (D_{4h}) which would both be found near 306 cm^{-1} in the absence of coupling. We can describe qualitatively the expected behavior as follows: Assuming energies of $\omega_{\text{CF}}=304\ \text{cm}^{-1}$ and $\omega_{\text{ph}}=308\ \text{cm}^{-1}$ for the unperturbed CF and phonon excitations, they now appear at low temperature at $\omega_2=274\ \text{cm}^{-1}$ and $\omega_1=331\ \text{cm}^{-1}$ due to the mixing and splitting. Since the coupling changes with increasing temperature, the splitting as well as the intensity of the CF-like lower peak decrease. For ^{18}O, the unperturbed phonon frequency shifts down by 6% and is hence lower than the unrenormalized CF frequency (which should not depend significantly on isotopic substitution) so that now the *upper* peak is CF-like and becomes stronger with decreasing temperature.

For the calculation of the spectral function of the coupled system, one has to take into account that a phonon extending over many unit cells interacts with localized CF excitations. The five different CF states are thermally populated with occupation fractions $p_1,\dots,p_5$ determined by Boltzmann statistics. Although both relevant CF states are doublets, only one of the possible four transitions between them (B_{1g}, B_{2g}, and E_g, the latter is doubly degenerate) has B_{1g} symmetry, so that there exist one B_{1g} phonon and one B_{1g} CF excitation per unit cell.

Two different Feynman diagrams have to be considered.

(i) An initial state $|n,0\rangle$ consisting of a phonon state with quantum number n and the distribution of CF states in thermal equilibrium undergoes a virtual transition to the $|n-1,+\rangle$ state by annihilating one phonon and by simultaneously generating a CF excitation from *level 1* to *level 4* in one unit cell and then returning to the initial state. The matrix element is in this case $V\sqrt{n}$. This process is possible only in the Np_1 unit cells where the CF ground state (*level 1*, N is the number of unit cells in the crystal) is occupied. In the random-phase approximation (RPA) we find[9] an effective interaction matrix element between the $|n,0\rangle$ and the $|n-1,+\rangle$ states of $V(np_1)^{1/2}$.

(ii) The same $|n,0\rangle$ state could also virtually go to the $|n+1,-\rangle$ state by generating one more phonon while at the same time relaxing in one unit cell a *level-4* state to the *level-1* CF ground state and returning to the initial state. This process, however, is only allowed in the Np_4 unit cells where the fourth CF level is occupied. We finally obtain[9] in the RPA for the effective matrix element $V[(n+1)p_4]^{1/2}$.

Using as a basis the $|n+1,-\rangle$, $|n,0\rangle$, and $|n-1,+\rangle$ states, we obtain[9] for each phonon quantum number n a three-band model with a Hamiltonian

$$H^n=H_0^n+H_1^n=\begin{pmatrix}(n+1)\omega_{\text{ph}}-\omega_{\text{CF}} & 0 & 0\\ 0 & n\omega_{\text{ph}} & 0\\ 0 & 0 & (n-1)\omega_{\text{ph}}+\omega_{\text{CF}}\end{pmatrix}+V\begin{pmatrix}0 & [(n+1)p_4]^{1/2} & 0\\ [(n+1)p_4]^{1/2} & 0 & (np_1)^{1/2}\\ 0 & (np_1)^{1/2} & 0\end{pmatrix}, \tag{2}$$

where H_0 corresponds to the uncoupled system. This Hamiltonian can be diagonalized yielding eigenstates $|1^n\rangle$, $|2^n\rangle$, and $|3^n\rangle$ (connected with the unperturbed states by the eigenvector matrix $\tilde{a}^n$), with energies E_1^n, E_2^n, and E_3^n which depend on temperature via the p_i.

We can finally calculate the Raman spectrum under the following assumptions:

(i) On all R-1:2:3 materials with other rare earths R, no CF excitations could be directly observed with Raman scattering, although the process is allowed. We therefore assume that all Raman intensity originates from the phonon scattering only, through admixture of the $|n,0\rangle$ to the $|n+1,-\rangle$ and the $|n-1,+\rangle$ states. This is further justified by the fact that the intensity ratio of the two double-peak components does not depend on resonance conditions, i.e., laser wavelength,[9] whereas the intensity changes considerably relative to the other phonons.[13]

(ii) The intensity for Stokes scattering from an n state to an $n+1$ state is proportional to $n+1$.[14]

(iii) The phonon states are occupied according to Boltzmann statistics with occupation possibilities P_n.

The Raman spectrum is then

$$R(\omega)\sim\sum_{n=0}^{\infty}\sum_{i,j=1}^{3}P_n(n+1)(a_{2i}^{n+1}a_{2j}^{n})^2L_\Gamma(E_i^{n+1}-E_j^n), \tag{3}$$

where $L_\Gamma(E_i^{n+1}-E_j^n)$ stands for a Lorentzian line shape of half width at half maximum Γ at an energy position $E_i^{n+1}-E_j^n$ corresponding to a Raman active transition.

This line shape has been fitted to the low-temperature spectrum for the ^{16}O case (Fig. 2, left, bottom) when $P_0=1$, $P_1=0$, $P_2=0,\dots$ and $p_1=0.5$, $p_2=0,\dots,p_5=0$ and hence only the two terms with $n=0$, $j=2$, $i=2$ and $n=0$, $j=2$, $i=3$ contribute to Eq. (3). From the fits, we can obtain the physical parameters: $V=35\pm2\ \text{cm}^{-1}$ is determined by the splitting at 10 K, and the unperturbed frequencies $\omega_{\rm ph}=308\pm2$ cm^{-1} and $\omega_{\rm CF}=304\pm2$ cm^{-1} by the ratio of the two peak intensities at low temperature which is nearly unity. (The "center of gravity" does not shift by the mixing so that $\omega_{\rm ph}+\omega_{\rm CF}\approx282+334=616$ cm^{-1}. A larger difference $\omega_{\rm ph}-\omega_{\rm CF}$ would lead to a smaller mixing and a smaller intensity of the lower CF-like peak.) We chose $\Gamma=10$ cm^{-1}.

For elevated temperatures Eq. (3) predicts (dashed lines in Fig. 2) a strong broadening of the structure since also terms with $n>0$ and other i,j combinations come into play of which some have frequencies even below 274 and above 331 cm^{-1}. Simultaneously, the two low-temperature lines approach each other. This is qualitatively what we observe experimentally. However, the calculated spectral weight away from the center of the structure is at 250 K larger than measured.

These deviations disappear almost completely if we assume (solid lines in Fig. 2) that anharmonic interactions (proportional to $\langle u\rangle^4\sim T^2$ with an average phonon amplitude $\langle u\rangle$) reduce the effective matrix element according to a phenomenological form

$$\tilde{V}=V[1-(\kappa T)^2]\,, \qquad (4)$$

with $\kappa=2.6\times10^{-3}$ K^{-1}. This is reasonable since many higher-order processes with possibly resonating energy denominators have been entirely neglected in the formalism developed above. These corrections will be described in more detail in a subsequent paper.[9]

The strongest argument for the validity of our approach is that we can describe the effect in the ^{18}O material very well with the same parameters, i.e., $\omega_{\rm ph}(^{18}{\rm O})=\sqrt{16/18}\,\omega_{\rm ph}(^{16}{\rm O})=290$ cm^{-1}, $\omega_{\rm CF}=304$ cm^{-1}, and $V=35$ cm^{-1}. The theory then gives correctly the different amplitude ratio at low temperatures as well as the disappearance of the *higher* peak at elevated temperatures. We also find that the isotopic shift at low temperature (mixed quasiparticles) is only half that at room temperature, as observed experimentally.

With this model, we can also explain the observation of a double peak in the inelastic neutron scattering spectra by Allenspach *et al.*[2] If a phonon and a CF excitation couple, not only the "CF excitation" gains phonon character (and is hence seen in the Raman spectrum) but also the "phonon" gains CF character; a double peak in the spectra of neutron scattering by CF excitations is expected. We note, however, that this case is more complicated since one also has to consider the coupling to phonons away from the center of the Brillouin zone (BZ).[7] Even a crossing of CF and phonon energies in the BZ is possible, introducing also imaginary parts of the self-energies and hence additional broadenings.

In conclusion, we have demonstrated that the appearance of a double peak in Raman and neutron scattering spectra on $\rm NdBa_2Cu_3O_7$ can be quantitatively accounted for by assuming coupling and hence mixing between the B_{1g} phonon and a CF excitation of the same symmetry. We obtained values for the coupling matrix element $V=35$ cm^{-1} and for the unperturbed frequencies $\omega_{\rm ph}=308$ cm^{-1}, $\omega_{\rm CF}=304$ cm^{-1} which may be compared with calculations. The theory also describes correctly the surprising dependence of the spectra on oxygen isotopic substitution and temperature.

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