Phonon self-energy effects in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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We report on the observation of phonon self-energy effects in the vicinity of T_c in the organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, and their interpretation in the framework of strong electron-phonon coupling. The data qualify anomalous temperature dependence of the low-frequency phonons around and below T_c, and are consistent with an isotropic gap $2\Delta_0$ close to 2.8 meV. Significant frequency shifts are recorded which allow us to evaluate the electron-phonon coupling λ for energetically weak phonons. The subsequent calculated values agree well with a superconducting transition at $T_c \sim 11.6$ K.

In cuprate superconductors, Raman spectroscopy and neutron scattering were exploited to scrutinize the phonon anomalies and quasiparticle dynamics arising in the superconducting state.[1–3] The electronic dressing of the phonons,[4,5] as well as the nature of the order parameter Δ were examined in detail.[6,7] In particular, much effort focused on explaining strong variations in the phonon self-energy $\Sigma(\omega)$, which were regarded as meaningful for validating phonon-mediated pairing mechanisms.[8–10] Indeed, phonons which are strongly coupled to electronic excitations near the Fermi level are likely to be sensitive to the opening of the superconducting gap 2Δ. The outcome in Raman spectra is the concomitant appearance of asymmetrical Breit-Wigner-Fano shapes, anomalous damping, phonon hardening, and phonon softening below T_c. In the highest-T_c family of the organic superconductors (OSC's) κ-(BEDT-TTF)$_2X$ (where BEDT-TTF or ET is the bis(ethylenedithio)tetrathiafulvalene molecule) such investigations have been essentially precluded because of the extreme difficulty in measuring minute energy shifts below T_c. When the 2Δ pair-breaking peak occurs between 40–70 meV in cuprates, in organics one expects it to be lower by one order of magnitude, with low-energy optical phonons as small as 2.2 to 13 meV.[11,12]

Recently, claims for phonon hardening close to T_c were reported by two groups for κ-(ET)$_2$Cu(NCS)$_2$ ($T_c = 10.4$ K) and κ-(ET)$_2$Cu[N(CN)$_2$]Br ($T_c = 11.6$ K).[13,14] Beside these two experiments which characterized an anomalous behavior of Re$\,\Sigma(\omega)$, there has been no report that confirms phonon renormalization, and a model that offers a coherent interpretation is still lacking. The very existence of such events in OSC's is an issue of central interest. Thus, one may wonder whether the phonon self-energy $\Sigma(\omega)$ experiences sizeable shifts below T_c, and if so, whether such shifts have bearing on the understanding of organic superconductivity. The origin of the phonons possibly involved in such effects is also elusive. Finally, this would allow for an unprecedented evaluation of the coupling of the phonons with continuum states of the superconducting condensate.

These issues are addressed in this paper where an extensive analysis of anomalous temperature-dependent phenomena affecting the Raman spectrum of κ-(ET)$_2$Cu[N(CN)$_2$]Br is reported. Near T_c, our results provide evidence for a crossover region between the frequency softening of the lowest energetic phonon and the hardening of a limited number of phonons in addition to anomalous broadening. Thus, in contrast with previous reports, we deliver more stringent lower and upper limits of the gap energy $2\Delta_0$. Our interpretation is founded on extending the Zeyher and Zwicknagl (ZZ) theory[15] to an OSC. Experimental variations of Re$\,\Sigma(\omega)$ are used to directly infer partial electron-phonon coupling constants consistent with the observed critical temperature of 11 K.

The objects of investigation were diamond shaped, submillimetric, untwined, superconducting single crystals selected from the same crystallization batch, typically $0.3 \times 0.2 \times 0.05$ mm in size. Their habit was checked with x-ray diffraction. The crystallographic *a*, *c*, and *b* axes were ascertained parallel to the long and short diagonal of the diamond, and perpendicular to the (010) plane, respectively. The crystals were attached with a heat transfer compound near a nominal-temperature silicon diode in a vacuum loading, helium cooled, continuous flow shielded microcryostat. The lowest possible temperature reached with this device was 5 K$\sim T_c/2$. The Raman spectra were collected under a microscope (objective $\times 50$) by a triple grating spectrometer with a liquid-nitrogen cooled charge-coupled device detector. The excitation $\hbar\omega_L = 1.83$ eV from a Kr^+ laser was chosen to get optimal spectral resolution ($\delta\gamma \sim 0.2$ cm^{-1}).[16] To account for a possible spectrometer drift, a number of plasma-discharge lines were recorded before each measurement, and calibration corrections were added to frequency values when needed. Attention was paid to keep the laser power as low as possible ($\leqslant 2$ kW/cm^2) and to avoid sample heating.

Note that one should exercise extreme care when interpreting the Raman spectra since instrumental resolution and phonon bandwidth can have the same order of magnitude. Therefore, Lorentzian fits were discarded. In order to obtain reliable phonon frequencies $\bar{\omega}$ and widths Γ, we extracted the first and second moments $M_1 = \bar{\omega} = \Sigma\omega_i I_i/\Sigma I_i$ and $M_2 = \Gamma^2 = \Sigma(\omega_i - \bar{\omega})^2 I_i/\Sigma I_i$, where ω_i, I_i are the frequency and intensity of a given spectral channel, respectively, with summation extended around the spectral maximum. This procedure insures a parameter-free determination of $\bar{\omega}$ with controllable absolute errors[17] which in our case are typically twice the theoretical resolution of the spectrometer.

Raman spectra were recorded in (cc), (ac), and (bc) scattering (Fig. 1) and also from a crystal rotated in the (010)

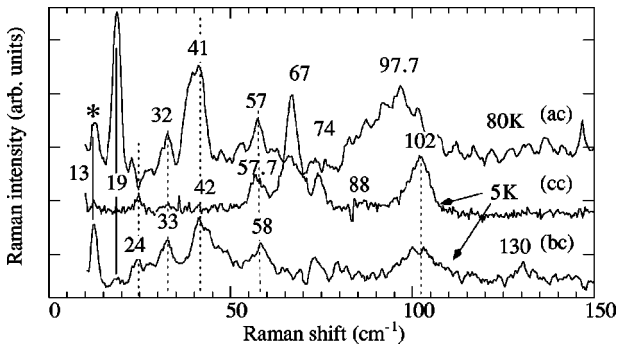

FIG. 1. Typical low temperature micro-Raman spectra obtained on a κ-$(ET)_2Cu[N(CN)_2]Br$ single crystal, recorded in (ac), (cc), and (bc) scattering. (*) Reference line.

plane. The good resolution of the bands at 57, 67, and 74 cm^{-1} in (cc) scattering allows us to follow their temperature dependence with sufficient accuracy. The previously unreported spectrum taken on the crystal slice [(bc)] is roughly similar to that taken in crossed (ac) polarization, the main difference being the relative intensities of the phonons at 19, 33, and 42 cm^{-1}. The (ac) and (bc) spectra confirm the existence of a phonon at 19 cm^{-1}, quite intense in (ac) scattering. The low-frequency phonons obey the selection rules of D_{2h} representations and are totally symmetric (A_g), except for the one at 19 cm^{-1} which belongs to B_{2g}. Separate experiments performed on ET crystals and thiocyanate salts indicated that the modes at 19 and 24 cm^{-1} are likely to stem from the anion sublattice while the strong mode at 33 cm^{-1} may originate from ET dimers.

The temperature dependences of Γ-point phonon frequencies $\bar{\omega}(T)$ and dampings Γ are plotted in Fig. 2. Table I summarizes the frequency shifts for all the phonons. The results single out phonon renormalization near T_c as shown by the increase of $\delta\bar{\omega}$ and $\delta\Gamma$ with respect to the bare values extrapolated from anharmonic curves.[18] $\delta\bar{\omega}$ finally exhibits much steeper jumps with greater magnitudes than in Ref. 14. Close to T_c we find that a number of phonons harden (at $\sim$24, 33, 44, 58, 67, 74, 102 cm^{-1}), while the shift of the most energetic phonons scales to zero (130, 153 cm^{-1}). This trend is accompanied by the broadening of the modes at 24, 33, 44, and 102 cm^{-1} below T_c, an observation unreported so far. Interestingly, the frequency and linewidth of the 19 cm^{-1} phonon display a steep increase around $T \sim T_c$ followed by monotonous decrease at lower temperatures (Fig. 2). This behavior is similar to that of the acoustic phonon reported at the same energy in κ-$(ET)_2Cu(NCS)_2$.[13]

We attribute these self-energy effects to the development of a temperature-dependent isotropic gap $2\Delta(T)$,[19] which spans the phonon energy $\hbar\omega$ below T_c. Our results corroborate what is expected in the frame of the clean-limit ZZ theory: since Γ is sensitive to the quasiparticle density of states at $\hbar\omega$, the condition $2\Delta(T) \leqslant \hbar\omega$ is satisfied near T_c. On cooling, the phonon hardens until $2\Delta(T) = \hbar\omega$. Then $\hbar\omega$ falls in the gap, $2\Delta(T)$ reaches a maximum exceeding the phonon energy, and consequently the phonon frequency softens whereas Γ rapidly decreases. One may recall the similar behavior of $\Gamma(T)$ for the 340 cm^{-1} phonon found in the $YBa_2Cu_3O_7$ high-T_c superconductor,[9,10] in which $2\Delta_0$ was determined at $\approx$440 cm^{-1}. The monotonous frequency drop

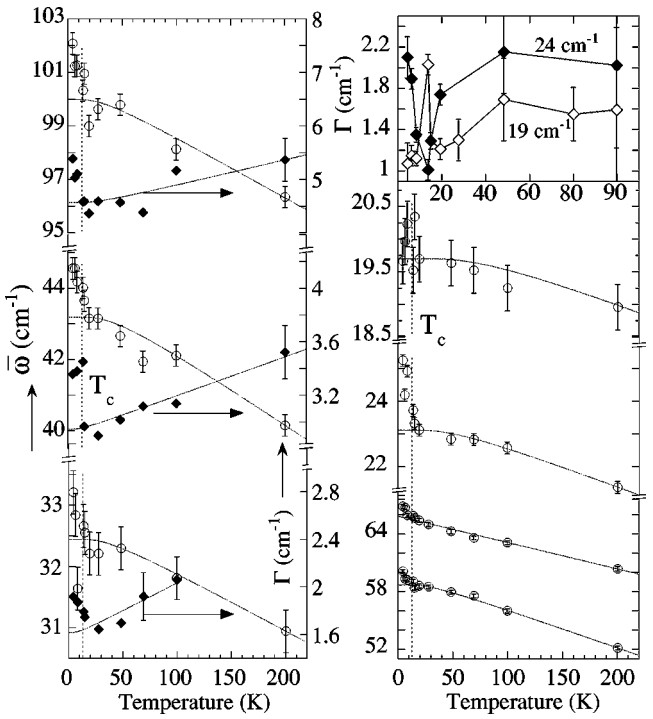

FIG. 2. Self-energy effects on the phonons at 19, 24, 33, 44, 58, 67, and 102 cm^{-1}. The circles are the frequencies, the diamonds the widths. The solid lines are anharmonical decays and guides to the eyes. The widths of the 19 and 24 cm^{-1} phonons (open and solid diamonds, respectively) are plotted against a double-sized temperature scale.

of this phonon[10] contrasts to the sharp-peak edge observed by us for the 19 cm^{-1} line and may be caused by a much shorter electronic mean-free path in cuprates. The behavior of the phonons above the gap ($\omega > 24$ cm^{-1}) is qualitatively different: again the prediction of the ZZ theory for $T < T_c$ is verified since Γ and $\hbar\omega$ monotonously increase. Therefore, we conclude that the low-frequency phonons in κ-$(ET)_2Cu[N(CN)_2]Br$ sense the opening of a gap $2\Delta_0$ in the range 2.3–2.9 meV.

Our strategy now will be to estimate the electron-phonon coupling for the phonons subjected to renormalization below

TABLE I. Frequency at 5 K, absolute and relative frequency shifts (hardening) as obtained from this work, real part of the electronic polarization function corrected for strong coupling and electron-phonon coupling constants.

$\bar{\omega}$ (cm^{-1})	$\delta\bar{\omega}$ (cm^{-1})	$\delta\bar{\omega}/\bar{\omega}$	$\Pi(\omega)/N(0)$	λ_i
19	0.6($\pm$0.2)	0.029	1.0600	0.11($\pm$0.04)
24	1.6($\pm$0.3)	0.068	1.0014	0.13($\pm$0.03)
33	0.6($\pm$0.4)	0.018	0.6474	0.057($\pm$0.038)
44	0.6($\pm$0.3)	0.014	0.4299	0.064($\pm$0.032)
58	1.4($\pm$0.2)	0.023	0.2862	0.16($\pm$0.02)
67	1.3($\pm$0.2)	0.020	0.2303	0.17($\pm$0.03)
74	0.9($\pm$0.4)	0.012	0.1979	0.12($\pm$0.05)
102	1.3($\pm$0.4)	0.014	0.1200	0.19($\pm$0.08)
130	not detectable	0	0.0815	0
153	not detectable	0	0.0626	0

T_c by fixing the value of the gap parameter. The basic tool of our approach is the ZZ formalism, in which the optical phonon frequency shift $\delta\omega$ [$\mathrm{Re}\,\Sigma(\omega)$] and the broadening $\delta\Gamma$ [$-\mathrm{Im}\,\Sigma(\omega)$] below T_c are proportional to the real and imaginary parts, respectively, of the electronic polarization function $\Pi(\mathbf{q}=0,\omega)$:

$$\delta\omega - i\,\delta\Gamma = (\omega\lambda/2)\Pi(\mathbf{q}=0,\omega)/N(0). \tag{1}$$

On the right-hand side, ω is the phonon frequency in the normal metallic state, λ the dimensionless electron-phonon coupling constant for the given phonon,[20] and $N(0)$ denotes the one-spin density of states at the Fermi level. Providing $\delta\omega/\omega$ is measured and the polarization function is properly calculated, Eq. (1) directly affords the coupling constants $\lambda = 2(\delta\omega/\omega)/(\mathrm{Re}\,\Pi/N)$.

It is now well established that OSC's are good representatives of clean-limit superconductors, with an electronic mean-free path which exceeds considerably the correlation length.[21] In the simplest, clean, weak-coupling limit, the real part of the polarization function is given at zero temperature by:[15]

$$\frac{\mathrm{Re}\,\Pi(\mathbf{q}=0,\omega)}{N(0)} = \frac{\ln(2\overline{\nu^2} - 1 + 2\overline{\nu}\sqrt{\overline{\nu^2}-1})}{\overline{\nu}\sqrt{\overline{\nu^2}-1}}, \tag{2}$$

where $\overline{\nu}$ is the dimensionless frequency $\omega/2\Delta_0$. Here, we restrict ourselves to the expression valid for frequency hardening, i.e., $\overline{\nu} \geqslant 1$, which is the case of interest in this work. However, since Eq. (2) applies for weak coupling, the λ values would always be *underestimated*. Therefore, one should consider strong coupling effects if they do exist. They can be pictured by a smearing of the sharp features in $\Pi(\omega)$ around the pair-breaking edge 2Δ, and substantial reduction of the absolute values of the self-energy with respect to the weak-coupling limit.[15,22] Nicol *et al.*[23] have proposed an approximate but direct way to account for the strong coupling. We follow their procedure by renormalizing the right-hand side of the BCS formula (2) with a correction factor $(1+\lambda_{tot})^{-1}$ in which $\lambda_{tot} = \Sigma\langle\lambda_i\rangle_{BZ}$ stands for the total electron-phonon coupling resulting from average summation over all vibrational branches of the Brillouin zone.

In order to estimate the strong coupling correction we use the standard McMillan's formula[24]

$$\frac{k_B T_c}{1.14\hbar\omega_0} = \exp\left[\frac{-1.04(1+\lambda_{tot})}{\lambda_{tot} - \mu^*(1+(\langle\omega\rangle/\omega_0)\lambda_{tot})}\right], \tag{3}$$

which holds on condition that

$$\lambda_{tot} \leqslant 1.5. \tag{4}$$

The cut-off frequency ω_0 is taken at 100 cm^{-1}, corresponding to the limiting energy of Raman-active phonons subjected to renormalization below T_c. This choice means that in turn these phonons are able to mediate the electronic pairing. The parameter $\langle\omega\rangle/\omega_0$ depends on the electron-phonon spectral function $\alpha(\omega)^2F(\omega)$ and is bounded in the [0,1] interval. There is no firmly established value for the Coulomb pseudopotential μ^* in OSC's. In Ref. 25 the Eliashberg equation has been solved at different λ and μ^* for κ-$(\mathrm{ET})_2\mathrm{Cu}(\mathrm{NCS})_2$. It was demonstrated that the T_c-effective mass dependence is best reproduced assuming an effective attraction $\mu^* = -0.2$ and, therefore, an additional electronic pairing mechanism has to be involved. Instead, as far as we are going to estimate the extreme requirements for a purely phononic pairing, we will set a repulsive value $\mu^* = 0.1$, as already chosen in interpreting point-contact spectroscopy data.[26] For a $T_c \sim 11$ K, Eq. (3) yields $0.81 \leqslant \lambda_{tot} \leqslant 1.0$. Then, quantitatively, the condition (4) is satisfied and $0.50 \leqslant (1+\lambda_{tot})^{-1} \leqslant 0.55$.

We adopt a value of $2\Delta_0 = 2.8$ meV (22 cm^{-1}), and we correct the BCS polarization function Eq. (2) by the strong-coupling factor $(1+\lambda_{tot})^{-1} = 0.53$. We assume that $\Delta(T)$ opens completely at the lowest accessible temperature $T_{min} \sim T_c/2$, and that Eq. (2) gives correct results at this temperature. Accordingly, the absolute frequency shift $\delta\overline{\omega}$ of the phonons is calculated by a difference between the frequencies at 5 K and T_c. For the phonon at 19 cm^{-1}, we use again Eq. (2) with $\delta\overline{\omega}$ calculated at the frequency maximum just below T_c, taking, however, $2\Delta(T) = \hbar\overline{\omega} < 2\Delta_0$.

Table I presents the calculated values of the electron-phonon coupling constants λ_i for the low-frequency phonon branches. Assuming that the λ values for Γ-point phonons are uniformly spread over the Brillouin zone, one gets $\lambda_{tot} = 0.97 \pm 0.11$. This value lies at the upper limit estimated from McMillan's formula.

We now comment on the striking fact that calculated partial λ values are up to one order of magnitude greater than those of $YBa_2Cu_3O_7$.[9] This can be explained if one recalls that κ-$(\mathrm{ET})_2X$ superconductors are near the border of an insulator-metal (I-M) transition, which can be switched on by Cl or I substitutions for Br.[27] Therefore, it is plausible to expect that particular phonons can substantially modulate the electronic density of states leading to anomalous large λ.

Finally, we note that the low-frequency phonon spectrum of κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$ consists of many phonon branches: the correct number of intermolecular vibrations of the ET molecules is 48, in addition to 84 anionic vibrations of which ≈ 24 involve the heaviest atoms, and several low-frequency intramolecular ET vibrations.[28] Our estimate of partial λ values shows that *only* 8 phonon branches are sufficient to account for the magnitude of the total electron-phonon coupling. Thus, a precise assignment of these vibrations in the crystal would be required in any microscopic theory of organic superconductivity in this phase.

In summary, we have presented and interpreted anomalous variations of $\Sigma(\omega)$, which characterize the superconducting transition near T_c in κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$. The uncertainties in our measurements are clearly much lower than the observed effects. We provide evidence for large variations of phonon frequency and damping rate Γ across T_c when $\hbar\omega < 13$ meV. Below T_c, the phonon at 19 cm^{-1} softens and Γ decreases. Simultaneously, the phonons lying above 24 cm^{-1} harden while Γ increases. According to the ZZ theory, such a behavior calls forth the opening of a relatively isotropic gap between 19 and 24 cm^{-1} (2.4–3 meV). We have handled these self-energy effects within the frame of a self-consistent strong coupling scenario. Our quantitative analysis indicates that if a limited number of low energetical phonons in κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N}(\mathrm{CN})_2]\mathrm{Br}$ are coupled to

conducting electrons, the value (or at least the right order) of T_c can be well reproduced. However, we bear in mind that the assumption of a small variance of the coupling constants over the Brillouin zone is not settled yet, and that complementary spin-fluctuation exchange channels are likely to play a significant role in the pairing process.[29]

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[17] It is straightforward to obtain for the standard deviation of the first spectral moment the following formula: $\langle \Delta\omega^2 \rangle = \Sigma(\omega_i - \bar{\omega})^2 \langle \Delta I_i^2 \rangle / \Sigma I_i$. The standard deviation of the intensity in a given spectral channel is estimated assuming a Poisson distribution: $\langle \Delta I_i^2 \rangle \sim I_i$.
[18] The frequency temperature dependence in the normal state is $\omega_{anh} = \omega_0 + \omega_1[1 + 2n(\omega_2)]$; n is the Bose-Einstein factor, ω_0 and ω_1 the bare frequency and anharmonic correction at zero temperature, and ω_2 a characteristic frequency of the vibrational branches anharmonically coupled to the phonon. Similarly, the damping dependence reads $\Gamma_{anh} = \Gamma_0 + \Delta\Gamma[1 + 2n(\omega_0/2)]$ where Γ_0 is the nonphononic process damping, and $\Delta\Gamma$ the anharmonic contribution to the width, at zero temperature.
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