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Observation of superconductivity-induced phonon frequency changes in the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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Abstract. – Frequencies of transverse acoustic phonons were measured by inelastic neutron scattering on single crystals of the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. Significant frequency changes were observed for phonon energies close to the superconducting energy gap 2Δ on cooling the sample below the superconducting transition temperature $T_c = 9.15$ K. The observed relative shifts are large compared to those in the classical superconductor Nb and also larger than the shifts found recently in the high-T_c superconductor $YBa_2Cu_3O_7$.

In superconductors the opening of a gap in the electronic density of states at the superconducting transition temperature T_c results in changes of phonon frequencies and linewidths. Such changes were first observed by Axe and Shirane [1] in Nb_3Sn and later by Shapiro *et al.* [2] in Nb. The results of these studies support the generally accepted picture that in classical superconductors, superconductivity is phonon-mediated. In recent years superconductivity-induced phonon self-energy effects were also observed in a variety of high-T_c oxides, in particular in $YBa_2Cu_3O_{7-x}$ [3]-[5]. Although it cannot be said that these observations yield conclusive evidence that superconductivity is phonon-mediated also in the high-T_c materials, they do signify that the electron-phonon interaction is relatively strong.

In this letter, we describe inelastic neutron scattering measurements which have provided similar results for a member of another class of superconductors with moderate T_c values around 10 K, *i.e.* the organic charge-transfer salt κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ ((BEDT-TTF) denotes bis (ethylenedithio) tetrathiafulvalene). This material is characterized by a crystal structure consisting of alternating layers of metallic and insulating materials. The conducting planes are formed by overlapping π-orbitals between sulfur atoms of adjacent organic molecules. Accordingly, quasi–two-dimensional electronic properties have been observed both above and below the superconducting transition [6], [7], reminiscent of some of the layered high-T_c cuprates. As in the latter, the mechanism for the superconductivity in the organic compounds is still controversial. Arguments for an unconventional pairing mechanism, involving, *e.g.*, the exchange of antiferromagnetic spin fluctuations [8], are based on the observations that i) for some materials superconductivity emerges from a magnetically ordered state upon applying external pressure [9], [10] and ii) spin fluctuations are present in the metallic state above T_c [11]-[13]. Such a magnetic mechanism would imply a highly anisotropic order parameter with nodes along certain symmetry directions. For the present κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ salt and the related κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br system conflicting results have been reported as for the order parameter symmetry. While some experiments showed derivations from the BCS predictions [14]-[16] and were interpreted in terms of unconventional Cooper pairing, others were found to be in excellent agreement with an isotropic order parameter [17]-[19] suggesting a conventional phonon-mediated pairing. In a complex system like the present molecular conductor, this pairing interaction could be provided by the coupling of the charge carriers to acoustic modes, to librational modes or to intramolecular vibrations. Yamaji proposed a modified weak-coupling BCS mechanism in which the coupling to the intramolecular modes dominates the attractive interaction [20]. It is known from both theory and experiment [21]-[24] that the electrons in the highest occupied molecular orbitals of the BEDT-TTF molecule strongly interact with the totally symmetric A_g intramolecular vibrations. These studies identify the carbon-carbon and carbon-sulfur streching modes in the central part of the BEDT-TTF molecules as the strongest coupling modes.

While comparatively much data are available on the electron itramolecular-vibration coupling, very little is known on the coupling of the electrons to the intramolecular vibrations, *i.e.* the translational and librational lattice modes. The frequencies of some of these modes have been observed by Raman [25] and far-infrared [26] spectroscopies. The salient result of the present investigation is that the superconducting charge carriers in the κ-(BEDT)-TTF)$_2$Cu(NCS)$_2$ salt strongly couple to the acoustic phonons suggesting a substantial contribution to the attractive pairing interaction.

Deuterated single crystals of κ-(d$_8$-BEDT-TTF)$_2$Cu(NCS)$_2$ were prepared by a conventional electrocrystallization method with d$_8$-BEDT-TTF (Kokyo Kasei, $> 99\%$ deuteration), CuNCS, KNCS and 18-crown-6 ether in 1, 1, 2-trichloroethane and 10 mol% ethanol [27], [28]. The quality of the crystals was checked by neutron diffraction. The crystals selected for our measurements had a mosaic spread of less than 1°. The first run was performed on a crystal of about 4 mm^3. For later measurements a composite sample of about 6 mm^3 was used. The superconducting transition temperature was measured inductively using a SQUID. We find a nucleation temperature, defined as the intercept of the linear extrapolations from above and below the transition, of $T_c = (9.15 \pm 0.05)$ K.

The neutron measurements were performed on the 2T-triple-axis spectrometer located at the ORPHEE-reactor of the LLB at Saclay. Due to the very small size of the available samples, the measurements were only feasible by using horizontally and vertically focussing pyrolithic graphite crystals as monochromator and analyzer. Details of the instrument are described in [29]. The final energy was chosen in the range $E_F = 12.5$ to 14.7 meV, and a pyrolithic

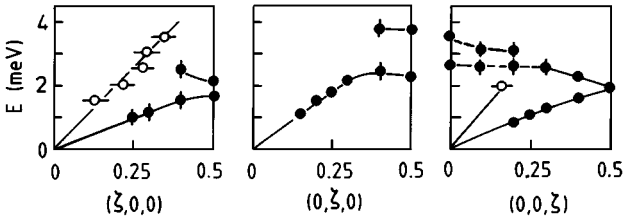

Fig. 1. – Phonon frequencies observed in longitudinal (L, open dots) and transverse (T, full dots) configuration at room temperature. Lines are a guide to the eye.

graphite filter was placed in the scattering beam to suppress higher-order contaminations. The energy resolution was typically 0.7 to 0.8 meV. For the low-temperature measurements, the samples were mounted in a cryostat with the (010)-axis vertical.

Exploratory measurements were performed at room temperature, the results of which are summarized in fig. 1. Transverse acoustic phonon branches in the $(\zeta, 0, 0)$, $(0, \zeta, 0)$ and $(0, 0, \zeta)$ directions could be followed up to the zone boundary. The energies of the zone boundary phonons were between 1.6 meV and 2.2 meV. We attempted also measurements of low-lying transverse optical phonons, but well-defined peaks were found only for energies up to ~ 2.5 meV. Our results indicate that for $E > 2.5$ meV, there is a large number of optical branches closely spaced in energy which interact with each other. The slope of the longitudinal acoustic branches in the $(\zeta, 0, 0)$ and the $(0, 0, \zeta)$ directions was found to be ~ 2.5 times higher than that of the corresponding transverse branches. As a consequence, the measurements could not be extended to the zone boundary.

The low-temperature measurements were much more difficult. Firstly, for typical phonon energies of interest there was a loss of an order of magnitude in intensity due to the Bose-Einstein factor. Secondly, spurious intensities caused much greater concern, not only because those associated with elastic scattering increase on cooling whereas phonon intensities decrease, but also because a higher precision was needed to detect the relatively small superconductivity-induced frequency changes. In the end, the choice was extremely restricted: meaningful data could be obtained only for momentum transfers in the vicinity of the (6, 0, 0) reciprocal lattice point for transverse phonons in the $[\zeta, 0, 2\zeta]$-direction (in reciprocal space this direction is practically parallel to the highly conducting $[0, 0, \zeta]$-direction in real space). In this direction, spurious intensities were found to cause the least trouble but also here phonon peaks below 2 meV could not be used for precise measurements of phonons energies. The maximum accessible energy transfer was 2.9 meV corresponding to the zone boundary phonon energy.

On cooling from room temperature to $T \sim 20$ K we found a gradual increase of phonon energies of about 15% which we attribute to anharmonic effects associated with the 4% volume contraction. Measurements below 20 K revealed a sudden increase of phonon energies at T_c which was most pronounced for the phonon with wave vector (−0.225, 0, 0.45) and energy 2.4 meV (see fig. 2 and 3). For smaller and larger energy transfers a smaller, if any, hardening was observed (fig. 4).

One might ask if the observed frequency changes are accompanied by changes in the phonon linewidth. We did not observe any significant change. This may be associated with the moderate resolution ($\Delta E/E \sim 30\%$) and low counting rates achievable in our experiment. The spectra shown in fig. 2 were fitted under the assumption of a constant linewidth.

We note that any cause other than superconductivity to account for the observed phonon frequency shift below $T = 9.15$ K, as, *e.g*, a structural phase transition, can be safely excluded as measurements of the specific heat [30], the thermal expansion [31] and the elastic

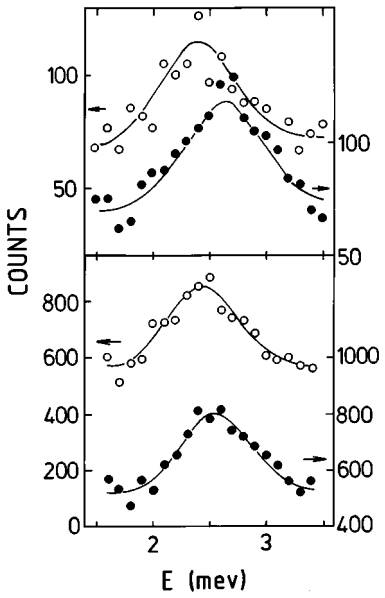

Fig. 2. – Constant-Q scans for sample 1 (above) and sample 2 (below) at temperatures slightly above T_c (sample 1: 10 K, sample 2: 11 K; open circles) and below T_c (sample 1: 7 K, sample 2: 6.4 K; full circles).

constants [32] performed in an overcritical field did not find any indication for an anomaly in the absence of superconductivity. We further note that the observed shifts are relatively large, being larger than those found in classical superconductors. It is the size of the effect rather than its mere occurrence which indicates that the electron-phonon coupling strength is large in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

Zeyher and Zwicknagl have calculated superconductivity-induced phonon shifts within the framework of Eliashberg theory [33], [34].These calculations were based on conventional strong-coupling theory assuming an isotropic s-wave gap and thus cannot be applied *a priori* to κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ for which also pairing states with non-zero angular momentum have been discussed. However, Yiang and Carbotte [35] have recently presented results for a d-wave superconductor which are not fundamentally different from those of Zeyher and Zwicknagl and we therefore think that the following qualitative conclusions may be drawn: A significant phonon shift can only be expected if the phonon frequency ω is close to the energy gap Δ. For $\hbar\omega < 2\Delta$, the phonon softens while for $\hbar\omega > 2\Delta$ it hardens (see fig. 8 in [34] or fig. 5 in [35]). Both phonon softening and phonon hardening have indeed been observed in $YBa_2Cu_3O_7$ [34]. From this general behavior we expect in our case a phonon softening for $\hbar\omega < 2.1$ meV. Unfortunately, this energy range was not accessible to us in our experiment. The fact that the maximum frequency shift of the 2.4 meV phonon seems to occur not at $T \sim 0$ but rather close to T_c might reflect that $E = 2.4$ meV is above 2Δ only close to T_c where the gap is not fully opened.

So, from our results described above we infer that in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, 2Δ must be close to 2.4 meV which implies $2\Delta/k_B T_c \sim 3.1$ (or somewhat larger when considering the fact that the maximum frequency shift was observed at a finite T). Since this number is close to the BCS ratio 3.52, one might conclude that this compound is a weakly coupled superconductor as has also been suggested by Lang *et al.* from measurements of the penetration depth [19].

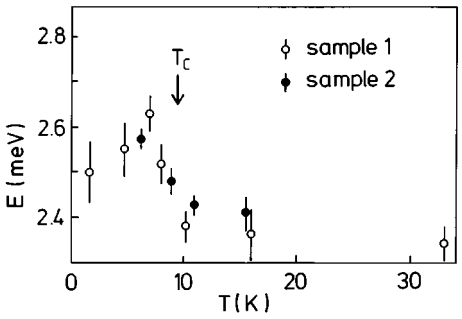

Fig. 3.

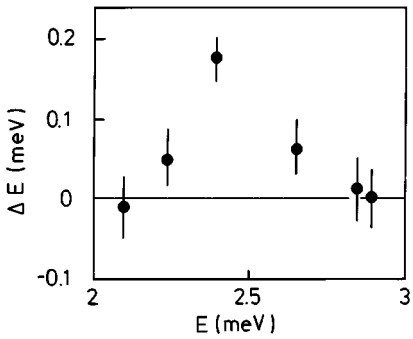

Fig. 4.

Fig. 3. – Temperature dependence of the energy of the transverse acoustic phonon with wave vector $q = (-0.225, 0, 0.45)$.

Fig. 4. – Observed frequency shifts ($E(T < T_c)$-$E(T > T_c)$) of transverse acoustic phonons in the $(-\zeta, 0, 2\zeta)$-direction *vs.* phonon energy.

On the other hand, in this extremely anisotropic compound the energy gap must be expected to be also anisotropic. Thus, depending on the symmetry of the affected phonon, the relevant gap coupling to this phonon may well be larger or smaller than the average value which enters the BCS relation $2\Delta/k_B T_c = 3.52$. Hence, our measurements cannot be used for a definitive determination of the coupling regime. But they provide a clear indication that in the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, the coupling between the superconducting charge carriers and the intermolecular phonons is strong.

To conclude, by means of inelastic neutron scattering we have measured the frequencies of transverse acoustic phonons in single crystalline κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. Investigations of their temperature dependences revealed a sudden increase in the phonon energies just below the superconducting transition temperature of $T_c = 9.15$ K. This phonon hardening was found to be most pronounced for the wave vector $q = (-0.225, 0, 0.45)$ and energy 2.4 meV. The large relative shifts, being in excess to those of the classical superconductor Nb, indicate a substantial coupling of the superconducting carriers to the acoustic modes. A strong, if not dominant, contribution of intermolecular modes to the pairing interaction is consistent with the result of isotope effect studies yielding i) the absence of a significant shift in T_c upon substituting ^{12}C only in the central carbon-carbon double bond by ^{13}C [36] but ii), more recently, a genuine T_c shift when replacing both four outer carbon atoms by ^{13}C and all eight sulfur atoms by ^{34}S [37].

REFERENCES

[1] Axe J. D. and Shirane G., *Phys. Rev. B*, **8** (1973) 1965.
[2] Shapiro S. M., Shirane G. and Axe J. D., *Phys. Rev. B*, **12** (1975) 4899.
[3] Macfarlane R. M., Rosen H. J. and Seki H., *Solid State Commun.*, **63** (1987) 831.
[4] Thomsen C. *et al.*, *Phys. Rev. B*, **37** (1988) 9860.
[5] Pyka N. *et al.*, *Phys. Rev. Lett.*, **70** (1993) 1457.
[6] Oshima K. *et al.*, *Phys. Rev. B*, **38** (1988) 938.
[7] Farrel D. E. *et al.*, *Phys. Rev. B*, **42** (1990) 8694.
[8] Hasegawa Y. and Fukuyama H., *J. Phys. Soc. Jpn.*, **56** (1987) 2619.

[9] Jérome D., *Mol. Cryst. Liq. Cryst.*, **79** (1982) 155.
[10] Welp U. *et al.*, *Phys. Rev. Lett.*, **69** (1992) 840.
[11] Jérome D. *et al.*, *Science*, **252** (1991) 1509.
[12] Mayaffre H. *et al.*, *Europhys. Lett.*, **28** (1994) 205.
[13] De Soto S. M. *et al.*, *Phys. Rev. B*, **52** (1995) 10364.
[14] Kanoda K. *et al.*, *Phys. Rev. Lett.*, **65** (1990) 1271.
[15] Le L. P. *et al.*, *Phys. Rev. Lett.*, **68** (1992) 1923.
[16] Mayaffre H. *et al.*, *Phys. Rev. Lett.*, **75** (1995) 4122.
[17] Harshman D. R. *et al.*, *Phys. Rev. Lett.*, **64** (1990) 1293.
[18] Klein O. *et al.*, *Phys. Rev. Lett.*, **66** (1991) 655.
[19] Lang M. *et al.*, *Phys. Rev. Lett.*, **69** (1992) 1443.
[20] Yamaji K., *Solid State Commun.*, **61** (1987) 413.
[21] Rice M. J. and Lipari N. O., *Phys. Rev. Lett.*, **38** (1977) 437.
[22] Kozlov M. E., Pokhodnia K. I. and Yurchenko A. A., *Spectrochim. Acta A*, **45** (1989) 437.
[23] Faulhaber J. C. R., Ko D. Y. K. and Briddon P. R., *Synth. Met.*, **60** (1993) 227.
[24] Sugai S. *et al.*, *Phys. Rev. B*, **47** (1993) 14374.
[25] Pokhodnia K. I. *et al.*, *Z. Phys. B*, **90** (1993) 127.
[26] Dressel M. *et al.*, *Physica C*, **203** (1992) 247.
[27] Sasaki T., Sato H. and Toyota N., *Solid State Commun.*, **76** (1990) 507.
[28] Sato H., Sasaki T. and Toyota N., *Physica C*, **185-189** (1991) 2679.
[29] Pintschovius L., *Nucl. Instrum. Methods A*, **338** (1994) 136.
[30] Andraka B. *et al.*, *Phys. Rev. B*, **40** (1989) 11345.
[31] Kund M. *et al.*, *Synth. Met.*, **70** (1995) 949.
[32] Yoshizawa M. *al.*, *Solid State Commun.*, **89** (1994) 701.
[33] Zeyher R. and Zwicknagl G., *Solid State Commun.*, **66** (1988) 617.
[34] Zeyher R. and Zwicknagl G., *Z. Phys. B*, **78** (1990) 175.
[35] Yiang C. and Carbotte J. P., *Phys Rev. B*, **50** (1994) 9449.
[36] Geiser U. *et al.*, *Synth. Met.*, **55-57** (1993) 2314.
[37] Kini A. M. *et al.*, *Physica C*, **264** (1996) 81.