

Effect of magnetic fluctuations on Raman scattering in κ -(BEDT-TTF)₂Cu(NCS)₂

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(Received 1 April 1998)

The temperature dependence of the intensity and frequency of two intense features in the Raman spectrum of κ -(BEDT-TTF)₂Cu(NCS)₂ have been measured. The spectra were taken with a Fourier Raman spectrometer equipped with an infrared laser. The two lines are due to a strongly resonant ν_9 (A_g) doublet, and a sharp line due to ν_{60} (B_{3g}). The frequencies of these modes are observed to soften below 80 K, in the temperature range where antiferromagnetic spin fluctuations have been observed with NMR, providing evidence of interactions between the phonons and the magnetism. [S0163-1829(98)50926-5]

BEDT-TTF [Bis(ethylenedithio)tetrathiafulvalene] is an electron-donor molecule, which has been the source of many charge-transfer salts with a variety of ground-state phenomena, including superconductivity and magnetic insulator. The κ -phase family of BEDT-TTF compounds, which include κ -(BEDT-TTF)₂X ($X = \text{Cu}(\text{NCS})_2$,¹⁻³ $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$,^{1,2,4-7} and $\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ ^{5,8,9}) are attractive for the study of the competition between superconductivity and magnetic ordering. The salts of $X = \text{Cu}(\text{NCS})_2$ and $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ are the well-known superconductors with transition temperatures of 10.4 and 11.6 K, respectively.¹⁰ However, the $\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ salt, which has a similar crystal structure to that of the $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ salt, is an insulator with antiferromagnetic ordering.^{5,8,9} This salt becomes a superconductor with a T_c of 12.8 K when under a pressure of 0.3 kbar.¹¹

Recently, ¹³C-NMR magnetic susceptibility, and Hall effect measurements of these compounds revealed the enhancement of antiferromagnetic spin fluctuations even in the superconducting salts in the temperature range of 50–80 K.¹⁻⁷ In κ -(BEDT-TTF)₂Cu(NCS)₂ many anomalies around 60 K have been reported, including resistivity,¹²⁻¹⁴ thermopower,^{12,14} electron-spin-resonance (ESR) spin susceptibility,¹⁵ and lattice expansion.¹⁶

An electronic band calculation of κ -(BEDT-TTF)₂Cu(NCS)₂ by Demiralp *et al.*¹⁷ found that the normal state of the system is a weakly antiferromagnetic conductor. As the temperature increases, the BEDT-TTF phonons couple to the electrons strongly and promote transitions between the two bands. These κ -type organic superconductors are similar to the high- T_c cuprate superconductors since both materials have a two-dimensional electronic structure and the interplay between magnetism and superconductivity.¹⁸

Raman scattering is sensitive to magnetic effects.^{19,20} It is therefore worthwhile to investigate the Raman scattering from κ -(BEDT-TTF)₂Cu(NCS)₂ in order to detect a correlation with the antiferromagnetic spin fluctuations between 50 and 80 K. To our knowledge, four papers have been published on the Raman scattering from κ -(BEDT-TTF)₂Cu(NCS)₂.²¹⁻²⁴ We have investigated the room temperature Raman spectrum with a Fourier Raman

spectrometer.²¹ The other three papers used a grating spectrometer with a visible laser, which is resonant with the intramolecular electronic excitation of the BEDT-TTF molecule around 20 000 cm^{-1} . Sugai *et al.*²² have measured the Raman spectra, covering the entire phonon frequency range, at 2, 20, 100, and 200 K. The Raman scattering was very weak and long data collection times, such as 24 h for one scan, were required. Zamboni and co-workers²³ have looked at selected regions of the Raman spectra from 50 to 400 cm^{-1} and from 1300 to 1550 cm^{-1} at 1.3 as well as 120 K. The low-frequency spectra below 160 cm^{-1} were measured by Sekine and co-workers²⁴ and a broad peak around 55 cm^{-1} was interpreted in terms of critical dynamics of the pseudo-spin-phonon coupled system.

However, none of these studies gave a detailed temperature dependence of the Raman features. In this paper we investigate the frequencies and intensities of the Raman scattering from a powdered sample of κ -(BEDT-TTF)₂Cu(NCS)₂ at temperatures between 10 and 293 K. Pronounced anomalies are observed around 60 K, the temperature reported for the magnetic fluctuations.

The measurements were performed with a Bruker RFS 100 Fourier Raman spectrometer, which operates with an infrared diode-pumped Nd:YAG laser with a wavelength of 1064 nm. Overheating was observed in the single crystals with laser power levels as low as 12 mW. The crystals were therefore ground with KBr powder and pressed into a hole in the copper sample holder to both reduce the laser heating and to provide a good thermal contact with the copper cold finger of the Air Products Heli-Tran refrigerator. The vacuum shroud had a room-temperature window of 2 mil polypropylene. The refrigerator unit was mounted on a platform in front of the spectrometer collection lens, and this platform could be adjusted in three perpendicular directions and about one vertical axis for sample alignment and signal optimization. A backscattering geometry was employed. The focal length of the collection lens was 50 mm. Two silicon diodes for temperature measurement and control were mounted on the cold finger, with one on the copper disc containing the powder sample, and immediately adjacent to it. The laser power was 70 mW. At each temperature we performed four runs of 500 scans each, taking a total of approximately one hour, and with a resolution of 4 cm^{-1} .

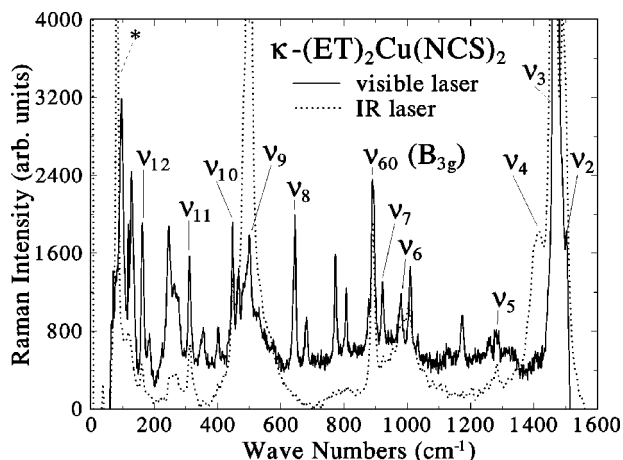


FIG. 1. The room-temperature Raman spectra of κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$, where BEDT-TTF is abbreviated as ET in the figure, taken with a visible laser (solid line) by use of a Raman microscope spectrometer at Argonne and an infrared laser (dotted line). Eleven of the 12 totally symmetric A_g modes and ν_{60} (B_{3g}) mode are labeled. The asterisk (*) indicates an atmospheric line.

The Raman spectra of BEDT-TTF compounds are similar and can be analyzed on the basis of the molecular vibrations of the BEDT-TTF molecule.^{21,25,26} Figure 1 shows the Raman spectra taken with a visible laser and with an infrared laser.²¹ Eleven of the twelve totally symmetric A_g modes, assuming D_{2h} molecular symmetry, are labeled for the visible-laser spectrum. One can see that the resonance conditions for the two lasers are quite different, producing quite dissimilar spectra. In particular the resonance of the infrared laser with the electronic excitation²³ at $11\,500\text{ cm}^{-1}$ produces a very intense feature at 500 cm^{-1} due to ν_9 (A_g). Figure 2 shows this infrared laser Raman spectrum between 400 and 600 cm^{-1} as a function of temperature. We can see that the intensity increases strongly with decreasing temperature until 70 K , after which it drops until 55 K and then

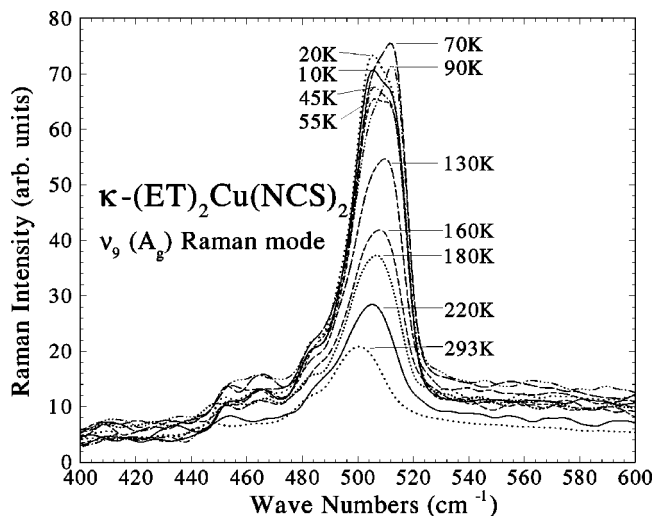


FIG. 2. The temperature-dependent Raman spectra of κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ between 400 and 600 cm^{-1} . The intensity of the ν_9 (A_g) Raman mode, a main feature of the spectra, has a strong variation with temperature.

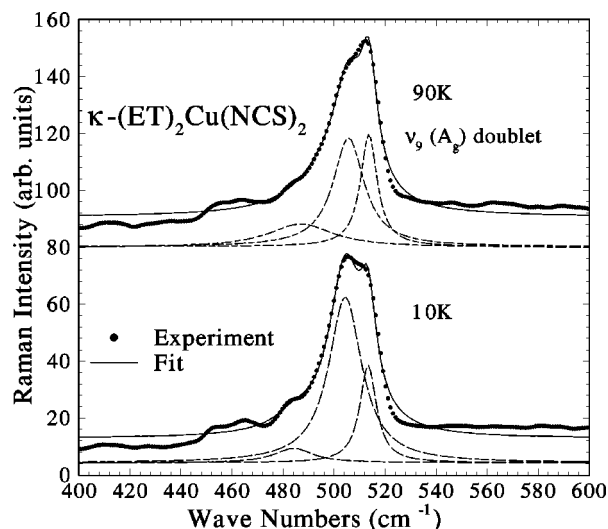


FIG. 3. The Raman spectra of the ν_9 (A_g) mode of κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ at 90 K and 10 K (dots) and the best-fitted results (solid lines) with three Lorentzians. The Lorentzian at 484 cm^{-1} is an unassigned Raman line clearly observed in the spectrum with the visible laser in Fig. 1.

grows again below 55 K . The frequency of the maximum also shifts down below 70 K . This unusual temperature-dependent shift of phonon Raman intensity has not been previously reported by others. In order to properly analyze the feature, it was fitted at each temperature to three Lorentzians, by a nonlinear least-squared method, and these may be seen at 90 and 10 K in Fig. 3. It is clear that ν_9 (A_g) is at least a doublet, and this is due to the two BEDT-TTF dimers in a unit cell. No assignment has yet been made of the third small resonance. [In the infrared spectra²¹ we have seen a quartet, which was due to ν_5 (A_g).]

The two components of this doublet behave differently as a function of temperature. Figure 4 shows the integrated intensity of both components versus temperature. The upper component (lower trace) is seen to have a broad maximum around 80 K and a minimum near 50 K . Figure 5 shows the

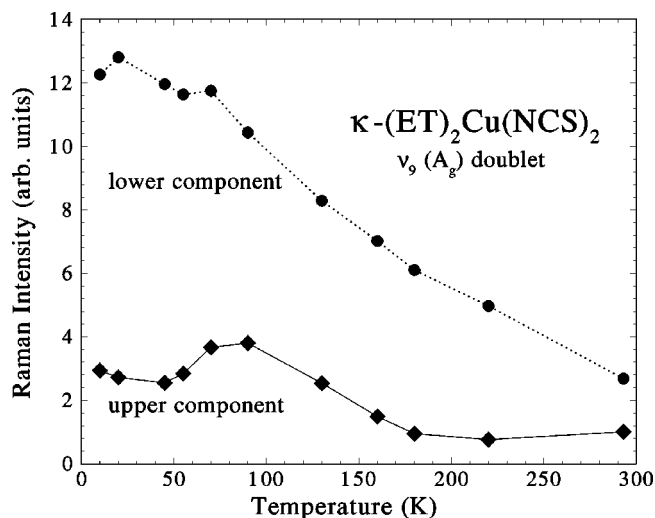


FIG. 4. The temperature dependence of the integrated intensities of the ν_9 (A_g) doublet: upper component (solid line) and lower component (dotted line).

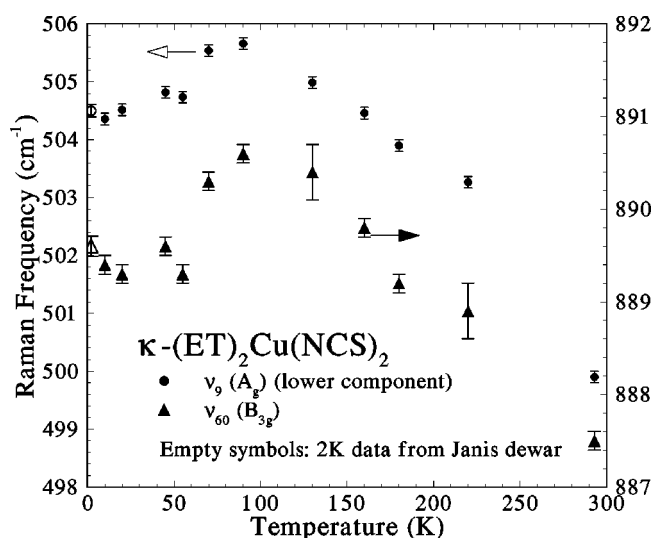


FIG. 5. Raman frequencies of the lower component of the ν_9 (A_g) doublet and the ν_{60} (B_{3g}) mode, as a function of temperature.

frequency of the lower component of the ν_9 (A_g) doublet, which is seen to soften below 80 K. On the same Fig. 5 is plotted the frequency of the sharp line at 890 cm^{-1} which is also resonant with the infrared laser, and which we have assigned to ν_{60} (B_{3g}) in the D_{2h} symmetry scheme. A pronounced softening below 80 K is again observed for this feature. This latter mode is anomalous in many ways, including a frequency increase of 2.2 cm^{-1} below T_c in $(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$.²⁷ No such increase below T_c has so far been observed in $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$ but that may be because we have not cooled it sufficiently slowly. We also investigated the strong features due to ν_2 , ν_3 , and ν_4 (A_g), around 1460 cm^{-1} , but found that at least six Lorentzians were needed to fit them, and the accuracy of the fits was therefore low. The behavior of the intensities and frequencies in Figures 4 and 5 are evidence of the interaction of the intramolecular phonons with the magnetic fluctuations occurring between 50 and 80 K.

Several papers have reported on phonon anomalies associated with magnetic effects. Litvinchuk, Thomsen, and

Cardona²⁰ have showed a remarkable correlation between the temperature-dependent softening of the phonon frequencies and the magnetic susceptibility in the superconductors $\text{YBa}_2\text{Cu}_4\text{O}_8$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.57}$ well above T_c where the ^{63}Cu nuclear-relaxation rate shows an anomaly. These softening were explained as an effect of the magnetic order above T_c on the phonon energy due to the opening of a spin pseudogap. Yamaguchi *et al.*²⁸ have reported an anomalous splitting of some phonon modes and their intensity variation with temperature for LaCoO_3 which shows an abrupt decrease of the magnetic susceptibility between 100 and 50 K. The intensity of one split mode increased while for the other two split modes it decreased below 100 K. The results were explained in terms of the Jahn-Teller effect. The temperature dependence of the integrated intensity of a broad Raman line in the magnetic semiconductors, europium chalcogenides, has been calculated and compared with the experimental results in terms of the one phonon-one spin mechanism,^{19,29} which predicts a decrease in the intensity as the temperature approaches T_c from above. For $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$, the frequency softening appears similar to that reported by Litvinchuk, Thomsen and Cardona²⁰ and is, therefore, probably due to the antiferromagnetic fluctuations. We note that this presents yet another similarity between the organic and high- T_c superconductors.

In summary, the Raman spectra of $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$, from 293 down to 10 K, have been measured using a Fourier Raman spectrometer. Several splittings of the Raman modes are observed. The temperature dependence of the Raman intensities and frequencies of two of these modes shows an anomaly around 60 K where antiferromagnetic spin fluctuations have recently been reported with NMR. There is therefore a correlation between the phonon and the magnetic anomalies.

The work at the University of British Columbia (UBC) was supported by Grant No. 5-85653 from the Natural Sciences and Engineering Research Council (NSERC) of Canada. The work at Argonne National Laboratory was performed under the auspices of the Office of Basic Energy Sciences, Division of Material Sciences, of the U.S. Department of Energy, Contract No. W-31-109-Eng-38.

¹A. Kawamoto, K. Miyagawa, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **74**, 3455 (1995).

²A. Kawamoto, K. Miyagawa, Y. Nakazawa, and K. Kanoda, Phys. Rev. B **52**, 15 522 (1995).

³K. Murata, J. Phys. I **6**, 1865 (1996).

⁴S. M. DeSoto, C. P. Slichter, A. M. Kini, H. H. Wang, U. Geiser, and J. M. Williams, Phys. Rev. B **54**, 16 101 (1996).

⁵M. A. Tanatar, T. Ishiguro, H. Ito, M. Kubota, and G. Saito, Phys. Rev. B **55**, 12 529 (1997).

⁶A. Kawamoto, K. Miyagawa, and K. Kanoda, Phys. Rev. B **55**, 14 140 (1997).

⁷H. Mayaffier, P. Wzietek, C. Lenoir, D. Jérôme, and P. Batail, Europhys. Lett. **28**, 205 (1994).

⁸U. Welp, S. Fleshler, W. K. Kwok, G. W. Crabtree, K. D. Carl-

son, H. H. Wang, U. Geiser, J. W. Williams, and V. M. Hitsman, Phys. Rev. Lett. **69**, 840 (1992).

⁹K. Miyagawa, A. Kawamoto, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **75**, 1174 (1995).

¹⁰J. M. Williams, A. J. Schultz, U. Geiser, K. D. Carson, A. M. Kini, H. H. Wang, W. K. Kwok, M. H. Whangbo, and J. E. Schirber, Science **252**, 1501 (1991).

¹¹J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. S. Crouch, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung, and M. H. Whangbo, Inorg. Chem. **29**, 3272 (1990).

¹²S. Gärtner, E. Gogu, I. Heinen, H. J. Keller, T. Klutz, and D. Schweitzer, Solid State Commun. **65**, 1531 (1988).

- ¹³L. I. Buravov, A. V. Zvarykina, N. D. Kushch, V. N. Laukhin, V. A. Merzhanov, A. G. Khomenko, and É. B. Yagubskii, *Sov. Phys. JETP* **68**, 182 (1989).
- ¹⁴K. Murata, M. Ishibashi, Y. Honda, N. A. Fortune, M. Tokumoto, N. Kinoshita, and H. Anzai, *Solid State Commun.* **76**, 377 (1990).
- ¹⁵S. Klotz, J. S. Schilling, S. Gärtner, and D. Schweitzer, *Solid State Commun.* **67**, 981 (1988).
- ¹⁶T. Doi, K. Oshima, H. Yamazaki, H. Maruyama, H. Maeda, A. Koizumi, H. Kimura, M. Fujita, Y. Yunoki, H. Mori, S. Tanaka, H. Yamochi, and G. Saito, *J. Phys. Soc. Jpn.* **60**, 1441 (1991).
- ¹⁷E. Demiralp and W. A. Goddard III, *Phys. Rev. B* **56**, 11 907 (1997).
- ¹⁸R. H. Mackenzie, *Science* **278**, 820 (1997).
- ¹⁹S. A. Safran, R. P. Silberstein, G. Dresselhaus, and B. Lax, *Solid State Commun.* **29**, 339 (1979).
- ²⁰A. P. Litvinchuk, C. Thomsen, and M. Cardona, *Solid State Commun.* **83**, 343 (1992).
- ²¹J. E. Eldridge, Y. Xie, Y. Lin, C. C. Homes, H. H. Wang, J. M. Williams, A. M. Kini, and J. A. Schlueter, *Spectrochim. Acta A* **53**, 565 (1997).
- ²²S. Sugai, H. Mori, H. Yamochi, and G. Saito, *Phys. Rev. B* **47**, 14 374 (1993).
- ²³R. Zamboni, D. Scheitzer, and H. J. Keller, *Solid State Commun.* **73**, 41 (1990).
- ²⁴T. Sekine, A. Ohmamiuda, Y. Tanokura, G. Saito, K. Ikeda, T. Nakamura, and T. Takahashi, *Synth. Met.* **70**, 981 (1995).
- ²⁵J. E. Eldridge, C. C. Homes, J. M. Williams, A. M. Kini, and H. H. Wang, *Spectrochim. Acta A* **51**, 947 (1995).
- ²⁶J. E. Eldridge, Y. Xie, H. H. Wang, J. M. Williams, A. M. Kini, and J. A. Schluter, *Spectrochim. Acta A* **52**, 45 (1996).
- ²⁷J. E. Eldridge, Y. Lin, H. H. Wang, J. M. Williams, and A. M. Kini, *Phys. Rev. B* **57**, 597 (1998).
- ²⁸S. Yamaguchi, Y. Okimoto, and Y. Tokura, *Phys. Rev. B* **55**, R8666 (1997).
- ²⁹N. Suzuki, *J. Phys. Soc. Jpn.* **40**, 1223 (1976).