PHYSICAL REVIEW B VOLUME 57, NUMBER 1 1 JANUARY 1998-I

T_c-dependent Raman scattering from a high-frequency phonon in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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(Received 31 January 1997; revised manuscript received 1 August 1997)

We report the temperature dependence of the frequencies of two high-frequency intramolecular modes in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br measured by resonant Raman scattering, with the use of a Fourier-transform spectrometer equipped with an infrared laser. One of these modes, that at 892 cm^{-1} and assigned to $\nu_{60}(B_{3g})$ exhibits an increase below T_c of 2.2 ± 0.7 cm^{-1} and 2.2 ± 0.4 cm^{-1} when measured in a Janis Dewar and in a Heli-Tran refrigerator, respectively. A smaller increase is observed in the deuterated sample and no increase is observed at all if the samples are cooled too rapidly. Two other modes, $\nu_3(A_g)$ at 1474 cm^{-1} and $\nu_9(A_g)$ at 503 cm^{-1}, show no such increase below T_c in the slowly cooled samples. We speculate that the normal electron-phonon interaction may not be responsible for the frequency increase but that the superconducting transition may involve a change in either the geometry or the arrangement of the BEDT-TTF molecules to which the particular mode is sensitive. [S0163-1829(98)07601-2]

I. INTRODUCTION

κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is an ambient-pressure organic superconductor with an inductive onset $T_c=11.6$ K.[1] The isostructural salt κ-(ET)$_2$Cu[N(CN)$_2$]Cl, where ET is the usual abbreviation for BEDT-TTF, on the other hand, is an insulator with antiferromagnetic ordering[2] at low temperatures after a metal-insulator transition at 50 K. Under a minimal applied hydrostatic pressure[3] of 0.3 kbar the latter becomes a superconductor at 12.8 K, the highest value for any organic compound, except the fullerenes.

Very recently Kawamoto and co-workers[4] reported that the *deuterated* κ-(ET)$_2$Cu[N(CN)$_2$]Br is in the critical region between the superconducting phase and the antiferromagnetic phase, with the crystals if they are slowly cooled containing both phases, but if they are rapidly cooled containing only the magnetic phase. In our Raman-scattering measurements on this material we have found one medium-strength high-frequency intramolecular mode near 890 cm^{-1} that is unusual in several respects, one of these being that the frequency *increases* upon deuteration by 9 cm^{-1} even though the mode does not involve the displacements of the hydrogen atoms. This suggests that the deuterated molecule has a slightly different conformation, and therefore this conformation may be playing a role in the competition between magnetic and superconducting behavior.

In this work we report that the frequency of this mode increases in the superconducting phase in the natural κ-(ET)$_2$Cu[N(CN)$_2$]Br compound, that it also increases but less so in the deuterated compound, and that no increase at all is seen if the sample is rapidly cooled. This behavior agrees with that reported by Kawamoto and co-workers[4] and implies that a molecular distortion accompanies the electronic phase transitions.

Pedron *et al.*[5,6] have reported a study of the Raman spectroscopy of some low-frequency phonons in κ-(ET)$_2$Cu[N(CN)$_2$]Br. They observed an increase in frequency of up to 3.2% for all of the phonons studied when the samples were cooled to 1.8 K. These phonons had frequencies ranging from 27 to 133 cm^{-1}, and the shifts were larger for the lower frequency modes. In Ref. 5 they compared their results to a strong electron-phonon coupling model and showed that they are more consistent with an *s* wave than with a *d*-wave gap function, and that the upper limit on the BCS energy gap would be 28 cm^{-1}.

Our measured shift of 2.2 cm^{-1} for the mode that we have assigned to $\nu_{60}(B_{3g})$ at 892 cm^{-1} is a much smaller percentage shift (0.25%) than those seen by Pedron *et al.*[5,6] but is very unusual for such a high-frequency phonon in a material with a small energy gap. No shifts were observed in the other strong features, which are due to A_g modes.

Few other Raman studies of these organic superconductors have been reported because the Raman scattering is very weak and long data collection times are required. This is due partly to the fact that the samples are black and tend to overheat. Thus low laser powers must be used. The only study of which we are aware that covers the entire phonon frequency range and was performed as a function of temperature is the one by Sugai *et al.*[7] on κ-(ET)$_2$[Cu(NCS)$_2$]. They reported no frequency changes at 4 K, which is below the transition temperature T_c of 10.4 K. A variable-temperature Raman study of $\nu_3(A_g)$ at 1473 cm^{-1} in κ-(ET)$_2$Cu[N(CN)$_2$]Br was reported by Truong *et al.*[8] and they saw large frequency shifts around 150 K. We, however, disagree with this result. Both Zamboni and co-workers[9] and Garrigou-Lagrange *et al.*[10] have also looked at selected regions of the Raman spectrum of κ-(ET)$_2$[Cu(NCS)$_2$] at low temperatures.

Several resonance Raman studies on α and β-(ET)$_2$I$_3$ have been reported, by Ludwig and co-workers,[11] Pokhodnia *et al.*,[12] Swietlik and co-workers,[13] and Sugai and Saito,[14] and also on β-(ET)$_2$IAuI, by Swietlik *et al.*,[15] and Ludwig and co-workers,[11] and one on α and β-(ET)$_2$IBr$_2$.[14] In α-(ET)$_2$I$_3$ (Refs. 11 and 12) and β-(ET)$_2$IAuI (Ref. 11) it was found that two low-energy phonon bands near 30 cm^{-1}, and assigned to librational modes of the ET molecule, vanished below T_c. This behavior agreed with a theoretical

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model of Behera and Ghosh,[16] but was not seen in κ-$(\mathrm{ET})_2\mathrm{Cu[N(CN)_2]Br}$.[5,6]

II. EXPERIMENT

The Raman data were obtained with the use of a Bruker RFS 100 Fourier Raman spectrometer, which operates with an infrared diode-pumped Nd:YAG laser with a wavelength of 1.06 μm. It is sometimes difficult to obtain good Raman spectra in a reasonable time from single crystals of organic conductors, when using the infrared laser, because it requires resonant Raman scattering to see the phonons, and sometimes there is little electronic absorption at the frequency of the infrared laser. For κ-$(\mathrm{ET})_2\mathrm{Cu[N(CN)_2]Br}$, however, there is strong electronic absorption, and the biggest problem was sample heating. Overheating was observed in the single crystals with laser power levels as low as 12 mW. We found, however, that the heating problem is considerably reduced if the crystals are ground into a powder with KBr, and then pressed into a conical copper sample holder, which then enabled us to increase the laser power and the Raman signal.

Two refrigerators were used. The first measurements were taken with an Air-Products Heli-Tran, with a copper cold finger and a room-temperature polypropylene vacuum-shroud window. The temperature range was from 295 K down to 7 K. 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 the sample. The laser power at 7 K was 15 mW. However, because of the uncertainty of the actual sample temperature, inherent in a cold finger arrangement, the lowest-temperature measurements were repeated in a second refrigerator, a Janis supervaritemp with quartz windows. In this system the lowest-temperature runs below T_c were performed with the sample completely immersed in superfluid liquid helium at 2 K, and the measurements above T_c were performed with the sample cooled by cold helium gas at 15 K. The quartz windows attenuated the signal more than the polypropylene window but this decrease was slightly compensated for by a permissable increase in the laser power to 20 mW at both temperatures. These refrigerators were mounted on different platforms in front of the spectrometer collection lens, with the sample at the focus. The focal length of the collection lens was 50 mm. A 180° backscattering geometry was employed. The resolution was 4 cm^{-1}.

Typically the frequency data points at the two lowest temperatures above and below T_c were the result of averaging 20 runs with 300 scans in each run, and the total time required being approximately three hours. The frequencies and the associated errors were obtained from the average and standard deviations of the peak frequencies obtained in the 20 runs. At all of the higher temperatures, a laser power of 50 mW was used and the spectra were an average of 1000 scans taken over a period of one half hour. The uncertainties were again obtained by averaging the data from many runs performed at selected temperatures.

The cooling rates varied from 10 K/min for the rapid cooling to 2.5 K/min for the slow cooling.

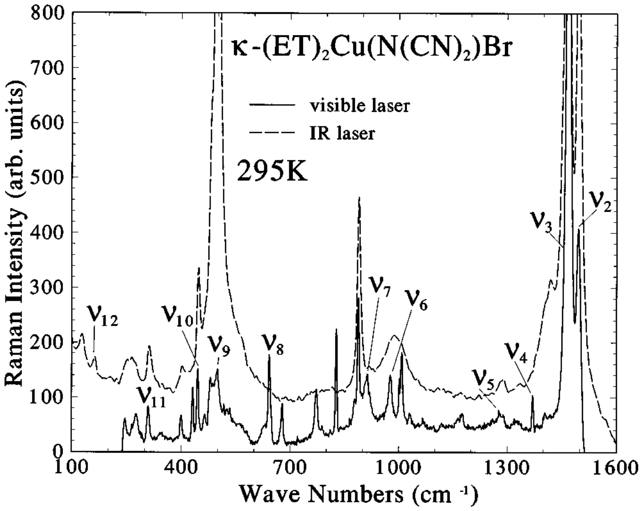

FIG. 1. The room-temperature Raman spectra of κ-$(\mathrm{BEDT\text{-}TTF})_2\mathrm{Cu[N(CN)_2]Br}$ taken with a visible laser (solid line) and with an infrared laser (dashed line), from 100 to 1600 cm^{-1}. Ten of the 12 assigned totally symmetric (A_g) intramolecular modes of vibration of the BEDT-TTF molecule have been labeled in the visible-laser spectrum, as well as $\nu_{12}(A_g)$ in the IR-laser spectrum.

III. RESULTS AND DISCUSSION

Figure 1 shows the room-temperature Raman spectra of κ-$(\mathrm{ET})_2\mathrm{Cu[N(CN)_2]Br}$ from 100 to 1600 cm^{-1}, taken with the infrared laser at the University of British Columbia and with a He:Ne laser in a Renishaw Raman microscope spectrometer at Argonne. The assignments of most of the totally symmetric (A_g) modes, labeled on the figure, follow from our previous studies with κ-$(\mathrm{ET})_2\mathrm{Cu[N(CN)_2]Br}$ (Ref. 17), κ-$(\mathrm{ET})_2[\mathrm{Cu(NCS)_2}]$,[18] and the neutral electron donor molecule BEDT-TTF (or ET),[19] in which both Raman and infrared spectra were taken of several isotopic analogs involving $^{13}\mathrm{O}$, $^{34}\mathrm{S}$, and $^{2}\mathrm{H}$. (A sketch of the atomic displacement vectors for the 12 A_g modes of ET, assuming D_{2h} symmetry may be seen in Ref. 17.) One can see that the resonant enhancement in Fig. 1 is quite different for the two lasers. In particular, the infrared laser misses $\nu_8(A_g)$ and several other unlabeled lines. The strongest enhancement in the infrared-laser spectrum is for $\nu_3(A_g)$ and $\nu_9(A_g)$, followed by $\nu_2(A_g)$, and the sharp unlabeled line at 890 cm^{-1}. In previous papers[17,18] we have argued that the best assignment for this last feature is $\nu_{60}(B_{3g})$, a nontotally symmetric mode. It does not appear in the Raman spectrum of neutral ET,[17,19] which is identical for both the visible and the infrared lasers since there is no resonance, and that would be unusual for an A_g mode. Furthermore it has isotopic frequency shifts that agree with those calculated for $\nu_{60}(B_{3g})$. A summary of the assignment arguments may be found in Ref. 18.

The electronic resonance that is enhancing the Raman scattering with the infrared laser appears to be the same electronic transition that produces the electron-phonon coupling responsible for the infrared activation of the gerade modes in the infrared spectra, since $\nu_3(A_g)$, $\nu_9(A_g)$, and $\nu_{60}(B_{3g})$ are also the strongest features in the infrared spectra. Figure 2 shows both the infrared conductivity[17] and the infrared-laser Raman spectrum of κ-$(\mathrm{ET})_2\mathrm{Cu[N(CN)_2]Br}$ in which these

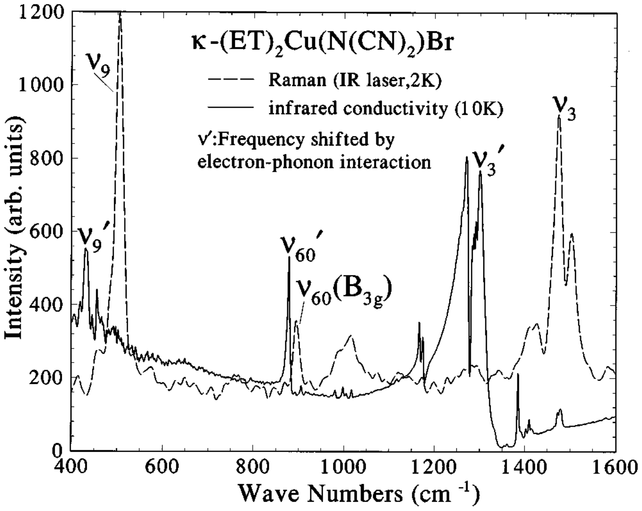

FIG. 2. A comparison of the infrared conductivity of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br at 10 K with the Raman spectrum at 2 K, taken with an infrared laser, of the same material. The three prominent features in each spectrum are due to $\nu_3(A_g)$, $\nu_9(A_g)$, and $\nu_{60}(B_{3g})$ and these have been labeled. The prime in the infrared label indicates that the feature has been shifted down in frequency due to the electron-phonon interaction. In the Raman spectrum $\nu_2(A_g)$ is also strong just above $\nu_3(A_g)$. In the infrared spectrum $\nu_3'(A_g)$ extends from 1200 to 1350 cm^{-1} and the fine structure is due to antiresonant interference with $\nu_5(A_g)$ that is a quadruplet at the same frequency.

three modes have been labeled and the clear similarity of the two spectra is evident. The primes on the infrared features indicate that they have been shifted down in frequency due to the electron-phonon interaction. The structure on ν_3' is due to the antiresonant interaction of $\nu_5(A_g)$, which is a quartet.[20]

The temperature dependence of the frequency of the feature due to $\nu_{60}(B_{3g})$ is shown in Fig. 3. The measured frequencies above and below T_c, when the sample is slowly cooled, are indicated for both refrigeration systems. The frequency increases are in very good agreement, being 2.2 ± 0.7 cm^{-1} for the Janis (from 892.4 ± 0.6 cm^{-1} to 894.6 ± 0.3 cm^{-1} at 2 K) and 2.2 ± 0.4 cm^{-1} for the Heli-Tran. (from 892.6 ± 0.3 cm^{-1} to 894.8 ± 0.3 cm^{-1} at 7 K). The reason for the low value of the error (only 0.3 cm^{-1}) is because of the high intrinsic wave-number stability of the Fourier-transform machine, due to the laser interferogram. It should be noted that these two measurements were performed on crystals made in different batches. The average increase is only 0.25% compared with 3.2% for the lowest measured frequency mode at 27.4 cm^{-1}, down to 0.6% for the highest frequency mode measured by Pedron *et al.*[5,6] at 133.5 cm^{-1}, but it is certainly statistically significant and unusual for such a high-frequency mode.

Upon rapid cooling we measured 892.9 ± 0.3 cm^{-1} at 15 K and 893.0 ± 0.3 cm^{-1} at 2 K, indicating no shift (see Fig. 3). For the deuterated compound we measured 901.9 ± 0.2 cm^{-1} at 15 K and 902.8 ± 0.2 cm^{-1} at 2 K, a superconductivity-induced shift of 0.9 ± 0.3, nearly one half of the shift seen in the natural compound. Notice the *positive* 9.0 cm^{-1} isotope shift, which was mentioned earlier. All of these results show that the effect is due to the superconductivity transition and agree with the results reported by Kawamoto and co-workers,[4] even though our cooling rates are different from theirs and their measurements were performed on only the deuterated samples.

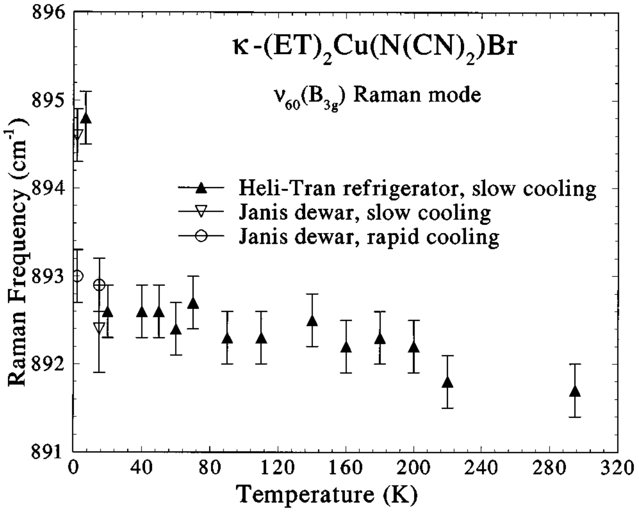

FIG. 3. The Raman frequency as a function of temperature of the feature due to $\nu_{60}(B_{3g})$ in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br measured with an infrared laser in a Fourier-transform spectrometer. Independent measurements, taken in a Janis Dewar at 2 and 15 K, above and below T_c at 11.6 K, are included. The frequency increases below T_c were obtained when the samples were slow cooled. The results of rapid cooling are also shown.

The temperature dependence of the frequencies of one of the stronger features in our Raman spectra of κ-(ET)$_2$-Cu[N(CN)$_2$]Br, that due to $\nu_3(A_g)$, is shown in Fig. 4. The frequency increases almost linearly over the entire range with no obvious discontinuities. The Heli-Tran. data show a possible increase below T_c but the Janis data confirm that this is not the case. Likewise no increase was observed with the Janis refrigerator below T_c for the other strong mode $\nu_9(A_g)$, at 504 cm^{-1}. (The data in Fig. 4 for $\nu_3(A_g)$ around 150 K disagree with those presented in Ref. 8, but those authors were working with a single crystal, which displayed a close doublet, and this is difficult to work with unless the signal-to-noise ratio is very good.)

Superconductivity-induced changes in phonon frequencies are of course evidence for electron-phonon coupling. Such changes are also seen in the high-T_c superconductors. Thomsen *et al.*[21] and Friedl, Thomsen, and Cardona[22] used the temperature dependences of the frequencies and linewidths of the Raman-active phonons to obtain an estimate for the superconducting gap in several RBa$_2$Cu$_3$O$_7$ compounds, where R is a rare-earth element, using the predictions of a strong-coupling model.[23] Altendorf *et al.*[24] looked at these changes as a function of oxygen concentration. In M$_3$C$_{60}$, on the other hand, Raman studies by Zhou *et al.*[25] and Brocard *et al.*[26] show weak or no temperature dependence of the high-frequency intramolecular modes through T_c. Zhou *et al.*[25] state that this is consistent with the fact that the frequencies of the modes are much greater than the energy of the superconducting gap. Since we also observed no temperature dependence of the frequencies of our high-frequency A_g modes, $\nu_3(A_g)$ and $\nu_9(A_g)$, perhaps the nor-

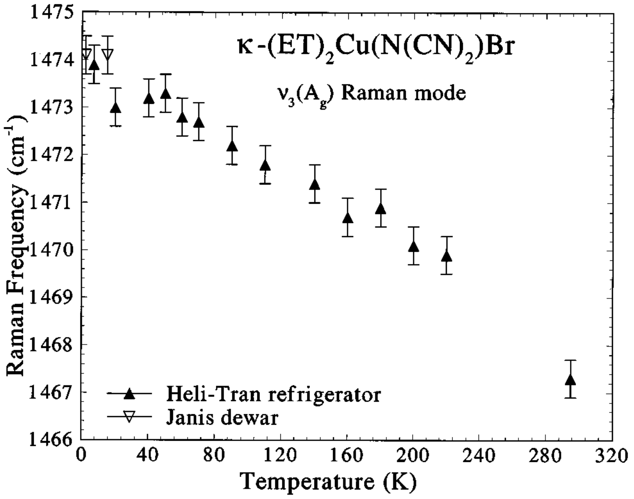

FIG. 4. The Raman frequency as a function of temperature of the feature due to $\nu_3(A_g)$ in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br measured with an infrared laser in a Fourier-transform spectrometer. Independent measurements, taken in a Janis Dewar at 2 and 15 K, above and below T_c at 11.6 K, are included. No increase below T_c is observed.

mal electron-phonon coupling does not explain the increase in the frequency of $\nu_{60}(B_{3g})$.

Figure 5 shows a sketch of $\nu_{60}(B_{3g})$ (with the assumption of planar D_{2h} symmetry). The manifestations of this mode are unusual for several reasons. First, it is strongly activated in the infrared spectra of the conducting ET salts (along with other much weaker B_{3g} modes) whereas theory predicts activation of only the A_g modes. Second, it is absent in the Raman spectrum of the neutral ET compound, but appears strongly in the spectra of the conducting salts. Third, it has this superconductivity-induced frequency increase reported here. Fourth, the mode frequency is almost constant from 15 to 295 K, decreasing by only 1 cm^{-1} compared with 7 cm^{-1} for $\nu_3(A_g)$ (see Figs 3 and 4). Finally, it has a *positive* isotopic frequency shift of $+9$ cm^{-1} upon deuteration of the ET molecule [also reported here and seen in the infrared,[20] where it was originally assigned to $\nu_{49}(B_{2u})$].

The infrared activity and superconductivity-induced frequency increase imply a strong coupling of $\nu_{60}(B_{3g})$ to the electrons, whereas the T-independent frequency implies a relatively weak coupling to the lattice. The positive isotope shift may also imply that upon deuteration the equilibrium geometry of the ET molecule or the arrangement of the ET molecules in the crystal change slightly in a way that increases the frequency of $\nu_{60}(B_{3g})$. This change may come about through a change in the electronic bandwidth as suggested in Ref. 4. This same change also affects the superconductivity and magnetic transitions. $\nu_{60}(B_{3g})$ involves the inner-ring double-bonded carbon sites as shown in Fig. 5. The same atoms are involved in $\nu_6(A_g)$, $\nu_{58}(B_{3g})$, and $\nu_{59}(B_{3g})$. These three modes are very close in frequency and are responsible for the broad feature centered at 1000 cm^{-1} in the IR-laser Raman spectra of Figs. 1 and 2. This feature grows at low temperature and also appears to be sensitive to T_c but our signal-to-noise ratio is insufficient to extract the three peaks and follow their frequencies through T_c. Nevertheless it is another indication that the superconducting transition may involve a rearrangement of the ET molecule that affects the inner-ring carbon atoms.

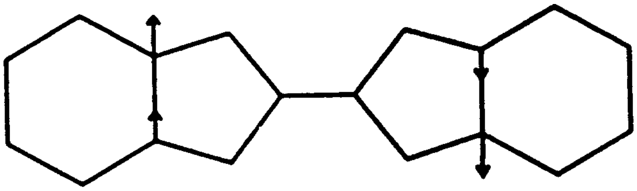

FIG. 5. The atomic displacement vectors for the $\nu_{60}(B_{3g})$ normal mode of vibration, assuming D_{2h} point-group symmetry.

IV. CONCLUSION

In conclusion, therefore, we have measured a significant increase in the frequency of a mode at 892 cm^{-1}, which we have previously assigned to $\nu_{60}(B_{3g})$, in the infrared-laser Raman spectrum of κ-(ET)$_2$Cu[N(CN)$_2$]Br below the superconducting transition temperature. The increase is only half as much in the deuterated compound and disappears if the sample is cooled too rapidly, confirming the dependence of the increase on the superconductivity. This increase is unusual for such a high-frequency phonon in a material with such a small energy gap. Since no increases are observed in the other high-frequency phonons in the spectrum, we speculate that below T_c the geometry or the arrangement of the ET molecules may change in a way that affects this particular mode of vibration.

ACKNOWLEDGMENTS

The work at 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.

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