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The correlation of lattice phonon frequencies with the superconducting transition temperatures of some (BEDT-TTF) salts

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The far-infrared powder absorption spectra, between 10 cm^{-1} and 350 cm^{-1}, of seven BEDT-TTF salts that exhibit superconductivity at or near ambient pressure, have been measured as a function of temperature, between 5 K and 300 K. The temperature dependences of the peak frequencies, along with the measured deuterium isotopic frequency shifts, separated the lattice from the internal modes. The frequencies of the observed lattice modes were found to increase with T_c in the three κ-phase salts in agreement with the reduced volume of the unit cell, and to have a mixed response in the three β-phase compounds. Furthermore, the general range and magnitude of the frequencies in the higher-T_c κ-phase compounds were found to be larger than in the lower T_c β-phase compounds. Consequently, no evidence was found for a correlation between higher values of T_c and a softer lattice in these organic superconductors.

1. Introduction

In a recent article by Williams et al. [1] are listed the forty presently-known organic superconductors. These have all been discovered in just over the past decade, beginning with $(TMTSF)_2PF_6$ at 0.9 K under an applied pressure of 10 kbar [2]. While the TMTSF donor molecule has produced seven superconductors, only $(TMTSF)_2ClO_4$ is an ambient-pressure superconductor, with a T_c of 1.4 K. The BEDT-TTF donor molecule, on the other hand, has been the source of twenty superconductors, most of them at ambient pressure, and among this family are those with the highest value of T_c. These are κ-$(ET)_2Cu(NCS)_2$ with $T_c=10.4$ K [3] (ET is the common abbreviation for BEDT-TTF), κ-$(ET)_2Cu[N(CN)_2]Br$ with $T_c=11.6$ K [4,5], and κ-$(ET)_2Cu[N(CN)_2]Cl$ with $T_c=12.8$ K at 0.3 kbar

[6]. There are several crystallographic phases adopted by the highly anisotropic and layered ET compounds, but the most common are the β-phase and the κ-phase. In the β-phase materials the two-dimensional layers of ET molecules, which are sandwiched between layers of anions, contain molecules whose planes are all parallel, whereas in the κ-phase materials the molecules are arranged in dimer pairs with alternating orthogonal orientation. In the course of attempting to synthesize materials with higher T_cs it was observed that there was a correlation between T_c and the unit-cell volume in the three isostructural β-phase superconductors β*-$(ET)_2I_3$, β-$(ET)_2AuI_2$, and β-$(ET)_2IBr_2$ [7,8]. More recently, Saito et al. [9] have included a few more ET superconductors, and have obtained the same correlation when T_c is plotted versus "effective volume", although the correction for the anion volume is not precise and the validity of this approach has not been proven. Fleming et al. [10] report a similar correlation for the cubic (isotropic) M_3C_{60} family of superconductors.

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In the *weak coupling BCS limit*, one can write

$$T_c \sim \theta_D \exp\left(-\frac{1}{\lambda}\right),$$ (1)

where θ_D is the Debye temperature and λ is the electron–phonon coupling constant, given by

$$\lambda = \frac{n(E_F)\langle I^2\rangle}{M\langle\omega^2\rangle},$$ (2)

where $n(E_F)$ is the density of states at the Fermi level, $\langle I^2\rangle$ is an electron–phonon matrix element averaged over the Fermi surface, M is the mass of the vibrating molecule and $\langle\omega^2\rangle$ is an average of the square of the phonon frequencies.

In the case of *strong coupling*, McMillan [11] found

$$T_c \sim \frac{\theta_D}{1.45}\exp\left(-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\,\lambda)}\right),$$ (3)

where

$$\lambda = 2\int_o^\infty d\omega\,\alpha^2 F(\omega)/\omega$$ (4)

and μ^* is the effective screened Coulomb interaction. In eq. (4), $F(\omega)$ is the phonon density of states and α^2 is a weighting factor proportional to the electron density of states at the Fermi level. In a subsequent treatment by Allen and Dynes [12] they showed that much better agreement between the various BCS superconductors and the theory could be obtained if the prefactor in eq. (3) was replaced by other forms, which involved various weighted integrals over the phonon densities of state.

The usual explanation for the "volume effect" on T_c, as discussed above, it that it is equivalent to negative pressure, which will increase the organic molecule interplanar distances, reducing both the transfer integral and electronic bandwidth, which in turn increases the density of states at the Fermi level, $n(E_F)$, causing T_c to rise (see eqs. (1) and (2)). An alternative explanation for these materials was proposed by Whangbo et al. [1,13,14] in which they postulated that the increase in λ results from the decrease in $\langle\omega^2\rangle$ in eq. (2), rather than an increase in $n(E_F)$. This decrease in $\langle\omega^2\rangle$ would result from a reduction in the intermolecular forces (softening)

in an expanded lattice. Certainly the decrease of T_c with applied pressure of the simple, nearly-free-electron BCS superconducting metals arises primarily from the pressure dependence of the phonon frequencies, since their electronic structure varies only slightly under pressure [15]. On the other hand, the increase in electron–phonon coupling, λ, between a good BCS superconductor like Nb and a better one like Nb$_3$Sn comes from an increase in $n(E_F)$ $\langle I^2\rangle$ rather than a decrease in $M\langle\omega^2\rangle$ [12]. This is due in part to the opposing effects of the phonon frequencies in λ and θ_D in eq. (1).

We therefore decided to measure the frequencies of some of the lattice modes of the ET superconductors by infrared spectroscopy in an attempt to see whether the higher values of T_c are accompanied by a lattice softening. The low site-symmetry of the ET molecules makes all of the lattice modes infrared active, and mixes the rotational and translational character, so that one may not also require Raman data. We emphasize, however, that the acoustic modes are not accessible to us and we recognize their importance in mediating conventional superconductivity, but the measurement of their frequencies would require inelastic neutron scattering. The lattice mode frequencies and eigenvectors depend on the crystal structure, which includes the number of formula units per unit cell, Z. A strict comparison can only be made, therefore, between isostructural crystals of the same phase, and even within this group between only those with the same Z. We have, therefore, investigated three κ-phase crystals and three β-phase crystals. A more general comparison will then be made between the compounds of these two distinctly different phases.

We have restricted our attention in this paper to the low-frequency lattice modes which should contribute the most to θ_D in eq. (1) and also to λ in eq. (2). It is possible that some high-frequency internal modes may also couple to the superconducting pairs, because their activated infrared intensity shows that they couple strongly to the normal charge carriers. A recent study [16], however, of the isotope effect in two ambient-pressure κ-phase ET superconductors, when two ^{13}C atoms are substituted for ^{12}C in the central double bond of the ET molecule, shows that the high-frequency totally-symmetric intramolecular mode near 1500 cm^{-1}, $\nu_3(a_g)$, which is the most

strongly activated mode [17], plays very little part in pair mediation.

2. Experimental

We have found in the past that a better signal-to-noise ratio in the far-infrared, when working with these organic conductors, is obtained by measuring the powder absorption rather than the reflectivity from single crystals [18]. (The crystals were prepared at the Argonne National Laboratory.) This is because the free carriers resulting from the high conductivity tend to screen out the small vibrational features. The powder method then allows one to probe the low-conductivity polarization (E perpendicular to the highly conducting planes), which is not possible by reflectivity, since the large crystal faces are parallel to the ET planes and the crystals are relatively thin. Furthermore, one can work with large powder samples, compared with small single crystals, resulting in a more intense signal. Accordingly, between 10 and 20 mg of material were ground in a Nujol mull (Aldrich #062977) for about 10 min and transferred to one side of a thin wedged TPX window [19].

The vibrational features sharpen as the temperature is decreased and we therefore mounted the samples in a Janis Supervaritemp Dewar, in which the cooling is achieved by cold vaporized helium gas. This eliminates the problem of thermal gradients associated with the sinking of a sample to a cold finger. The temperature was controlled to within 1 K by means of a PAR 152 temperature controller. The dewar windows were 0.75 in. diameter, 0.002 in. thick polypropylene. The dewar tail was positioned at the focus of one of the sample chambers of a Bruker IFS 113V Fourier spectrometer, and the detector was an Infrared Labs doped-germanium composite bolometer operating at 4.2. K. Spectra were typically obtained at 1 cm^{-1} resolution with 800 averaged scans taking a total time of 40 min. Background spectra were obtained from a clean TPX window in 10 min. The data between 15 cm^{-1} and 50 cm^{-1} were obtained using a 50 μm mylar beam splitter, while between 50 cm^{-1} and 350 cm^{-1} a 6 μm mylar beam splitter was used.

3. Results and discussion

Figure 1 shows the uncalibrated powder absorption coefficient at five temperatures between approximately 20 cm^{-1} and 350 cm^{-1}, for κ-(ET)$_2$Cu[N(CN)$_2$]Br. Several vibrational features are evident, and they sharpen at lower temperatures. The frequency of the peak of these features at 20 K are listed in table 1. (The data obtained at 5 K exhibited more noise than the others due to the appearance of small liquid helium droplets in the sample chamber, when operating near the boiling temperature). Figure 2 shows similar spectra for κ-(ET)$_2$Cu[N(CN)$_2$]Cl, in which the signal-to-noise ratio at the high-frequency end is improved over that in fig. 1. Both of these figures are used in order to point out the similarity between them at all temperatures. This means that the Cl salt has not undergone the reported [6] metal–insulator phase transition near 50 K, but has instead remained metallic and is superconducting at 5 K. The 0.3 kbar pressure required to suppress the insulating transition [20] is provided by the frozen mineral oil surrounding the powder particles in the Nujol mull. If no pressure were present, a semiconducting band gap would be clearly evident in the low-temperature spectra, in the
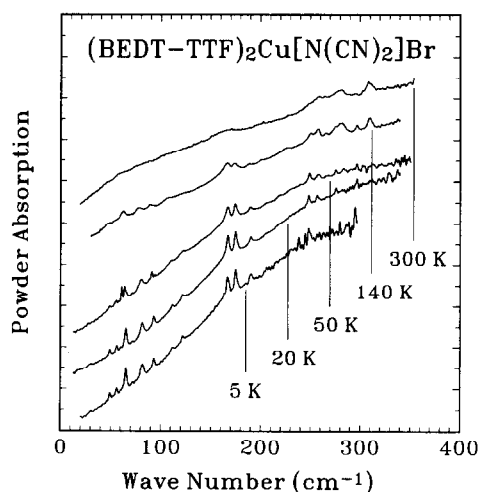

Fig. 1. The far-infrared powder absorption of κ-(ET)$_2$Cu[N(CN)$_2$]Br at five temperatures. The resolution is 1 cm^{-1}, and the spectra, displaced for clarity, are the logarithmic ratios of the transmission through a clear window to that of the transmission through the powder and window.

Table 1
The frequencies, in wavenumbers, of the powder absorption features at 20 K, of three κ-phase $(ET)_2X$ salts [a]

X = T_c =	$Cu(NCS)_2$ 10.4 K	$Cu[N(CN)_2]Br$ 11.6 K	$Cu[N(CN)_2]Cl$ 12.8 K at 0.3 kbar
Group			
1.	62.9 w	48.9 w ↓	74.2 vw ↑
	66.5 vw	55.9 w ↓	77.1 w ↑
	69.4 vw	65.1 s ↓	
2.	85.6 m	81.2 m ↓	86.3 s ↑
	91.6 m	93.0 m ↑	96.4 m ↑
3.	102.9 w	111.6 w	112.8 w ↑
		121.7 w	126.8 m ↑
4.	162.9 s	167.0 s ↑	168.7 m↑
	166.1 m	174.8 s ↑	178.1 s ↑
	173.3 w	190.2 m ↑	192.8 m ↑
5.		248.3 m	247.6 m
		256.7 w	257.7 w
		275.8 w	275.0 m
6.		297.0 w	296.5 m
7.			310 br

[a] ↑(↓) indicates an increase (decrease) in lattice mode frequency compared with the column to its left. vw means very weak, w weak, m medium, s strong and br broad.
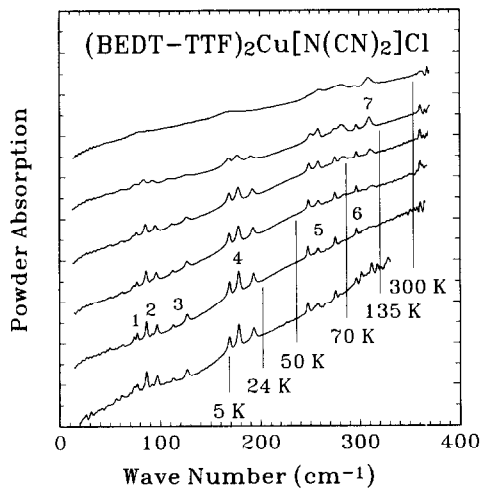

Fig. 2. The far-infrared powder absorption of κ-$(ET)_2Cu[N(CN)_2]Cl$ at six temperatures. The frozen Nujol mull prevents the metal – semiconductor transition at ∼ 50 K in favor of a superconducting ground state. The resolution is 1 cm^{-1} and the spectra, displaced for clarity, are the logarithmic ratios of the transmission through a clear window to that of the transmission through the powder and window.

form of reduced powder absorption below 1000 cm^{-1} [21]. The increasing slope of the spectra with lowered temperature is due to the higher conductivity in this region at low temperatures.

In order to separate the lattice modes from the internal modes, we plotted the frequencies of the features versus temperature, and also repeated the measurements on two of the compounds in which the eight hydrogen atoms of the ET molecule were replaced with deuterium. Figure 3 shows the temperature-dependence of the frequency of five stronger features in the Br-salt spectra of fig. 1. The lower three of these show the usual softening of a few percent, as the temperature is raised, associated with lattice modes. The top two show a constant or increasing frequency, which is the signature of an internal mode. Confirmation of this comes from the isotope shifts. Figure 4 shows the spectra of the protonated (h_8) and deuterated (d_8) Br salt at 20 K, with guide lines drawn between corresponding features in the two spectra. The frequencies of these features for this salt and the $Cu(NCS)_2$ salt are listed in table 2 along with the isotopic ratios $\bar{\nu}_h/\bar{\nu}_d$. The features are arranged somewhat arbitrarily into groups which are labelled 1 through 7 on fig. 2, which shows the most extensive spectra. Some of the components in these groups
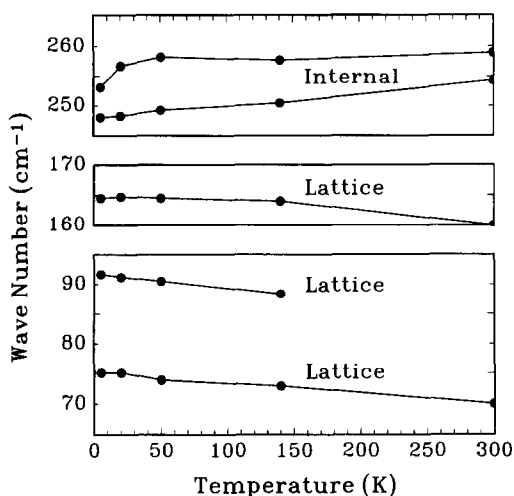
Fig. 3. The frequencies of the peaks of five of the larger features in the spectra of $(ET)_2Cu[N(CN)_2]Br_1$, (fig. 1), as a function of temperature. This temperature dependence, along with the measured isotope shifts of table 2 and fig. 4 help to identify the lattice and internal modes.
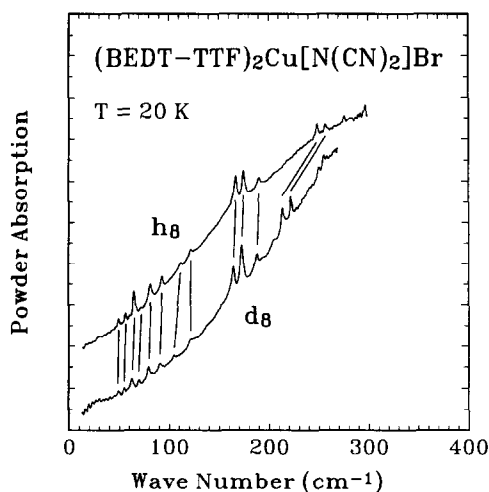

Fig. 4. The far-infrared powder absorption spectra of protonated and deuterated κ-$(ET)_2Cu[N(CN)_2]Br$ at 20 K. The lines correlate the features in the two spectra.

result from the large number of ET molecules per unit cell.

The expected isotopic ratios for translational and librational lattice modes, involving only the ET molecule, have been calculated and are listed in table 3. They range from 1% for the translational and R_z librations, to 3% for the other two librations. As already mentioned, the lattice modes will be a mixture of these degrees of freedom. The molecular point group symmetry is approximately D_{2h} if the ET molecule is considered to be flat. The rotations will transform according to the symmetric b_g irreducible representations, while the translations will transform according to the non-symmetric b_u representations. The site symmetry of the ET molecule in the salts investigated here is general (C_1) which will mix the b_g and b_u modes. A centre of inversion at the ET site (C_i) would be required to keep them separate. κ-$(ET)_2Cu(NCS)_2$ has a monoclinic space group $P2_1(C_2^2)$ with $Z=2$ and one layer per unit cell; κ-$(ET)_2[N(CN)_2]X$, $X=Br$, Cl, are orthorhombic with space group $P_{mna}(D_{2h}^{16})$ and $Z=4$ and there are two layers per unit cell; β-$(ET)_2X$ salts are triclinic with space group $P\bar{1}(C_i^1)$, $Z=1$ and one layer per unit cell. In table 2, therefore, the features in the first four groups are seen to have isotope ratios in the calculated lattice-mode range, with only one or two exceptions, and because of this, and the frequency temperature dependence, they are assigned to mixed lattice modes.

Group 5, in tables 1 and 2 and fig. 2 with a 16% isotope ratio, and the frequency temperature dependence shown in fig. 3 is clearly an internal mode, and is assigned to an *out-of-plane* b_{3u} mode, since there are no *in-plane* modes with this frequency and isotope shift in the results of the normal-coordinate calculations of Kozlov et al. [22]. We did not obtain an isotope shift for the feature labelled #6 and so are unable to assign it. The #7 feature in table 1 and fig. 2 however, which appears only at high temperatures at 310 cm^{-1}, has been seen by us before [17] and is the totally-symmetric internal mode $\nu_{11}(a_g)$. It is vibronically-activated and is therefore polarized in the highly-conducting plane. The optical activity is a result of charge oscillating between ET molecule dimers. Its appearance at high temperatures follows from the decrease of the underlying electronic conductivity in the conducting plane, which masks vibrational features at low temperatures.

Returning to table 1, which lists the frequencies of the vibrational features for the three κ-phase salts, we have indicated with an arrow whether the lattice mode frequencies (the first 4 groups) have increased or decreased with respect to those of the compound

Table 2
The isotopic frequency ratios at 20 K of two κ-phase $(ET)_2X$ salts

X	$Cu(NCS)_2^-$			$Cu[N(CN)_2]Br^-$		
	h_8	d_8	$\bar{\nu}_h/\bar{\nu}_d$	h_8	d_8	$\bar{\nu}_h/\bar{\nu}_d$
Group						
1.	62.9	62.4	1.008	48.9	49.4	0.990
	66.5	–	–	55.9	55.0	1.016
	69.4	68.7	1.010	65.1	62.7	1.038
2.	85.6	83.4	1.026	81.2	79.3	1.024
	91.6	93.8	0.098	93.0	90.9	1.023
3.	102.9	102.9	1.000	111.6	105.1	1.062
	–	–	–	121.7	122.0	0.997
4.	162.9	–	–	167.0	164.6	1.015
	166.1	163.9	1.013	174.8	172.6	1.013
	173.3	170.2	1.018	190.2	188.3	1.010
5.	–	–	–	248.3	213.1	1.165
	–	–	–	256.7	222.3	1.155

Table 3
Calculated isotope ratios of the lattice modes involving only ET
molecules [a]

Type of mode	Calculated $\bar{\nu}_h/\bar{\nu}_d$
Translational	1.010
Libration R_x	1.029
Libration R_y	1.031
Libration R_z	1.010

[a] The z-axis is along the central C=C bond. The y-axis is in the molecular plane, while the x-axis is normal to it.

to the left with the lower T_c. For the Br^- salt, compared with the $Cu(NCS)_2^-$ salt there is a mixture of increases and decreases, but because of the different crystal structure and Z, we feel the comparison is not valid. In a previous mid-infrared study [23] we found that the frequencies of the normally-active b_{2u} internal modes decreased slightly in the Br^- salt due to the looser packing in the conducting a–c plane, compared with the conducting b–c plane of the $Cu(NCS)_2^-$ salt (see table 4). The spacing $between$ the planes, however, is smaller for the Br^- salt than for the $Cu(NCS)_2^-$ salt and this will produce increases in some lattice frequencies. (The unit cell volume divided by Z is actually smaller for the Br^- salt, as opposed to statements in ref. [23] (see table 4.))

For the Cl salt, compared with the isostructural Br

salt, however, it is seen that all of the lattice mode frequencies increase. This follows naturally from the smaller unit cell volume, which would produce a stiffer lattice (see column 7 in table 4 for data measured at 127 K). For this group of three κ-phase compounds, therefore, in which T_c rises just over 2 degrees as the unit cell volume $decreases$ it appears that neither the electronic density of states nor lattice softness is responsible for this rise in T_c. It is possible that the θ_D prefactor is having an effect, but the mechanism is probably far more complicated.

The β-phase crystals that we have investigated are β-$(ET)_2IBR_2$ ($T_c=2.8$ K), β-$(ET)_2AuI_2$ ($T_c=5$ K) and β-$(ET)_2I_3$. The frozen mineral oil has probably again provided a pressure of at least 0.5 kbar, so that we have obtained the powder spectrum of β_H (or β^*)-$(ET)_2I_3$ with a T_c of approximately 8 K. As a possible check on this we also measured the spectrum of a sample of α_t-$(ET)_2I_3$, where α_t is the transformed α-phase with a T_c also near 7–8 K (see next paragraph). This transformation is accomplished by heating at 70°C for at least 70 h. Figure 5 shows the temperature dependence of the spectrum of β-$(ET)_2AuI_2$ and the features in the 20 K spectrum have again been labelled in groups. Figure 6 shows the 20 K spectra of all of the compounds investigated in this study. These are arranged in order of increasing T_c proceeding from the bottom to the top of the figure, with the three κ-phase compounds on

Table 4
Unit cell parameters and the superconducting transition temperatures of the $(ET)_2X$ salts investigated in this study

Salt	T_c (K)	T_{meas} (K)	a (Å)	b (Å)	c (Å)	V (Å³)/charge	V_{eff} (Å³) [a]	Z	Ref.
β-(ET)$_2$IBr$_2$	2.7	120	6.589	8.820	14.988	807.1	692	1	[b]
β-(ET)$_2$AuI$_2$	5	120	6.570	8.891	15.299	821.7	707	1	[c]
β-(ET)$_2$I$_3$	8.1 (β^*)	120	6.561	9.013	15.173	829.2	704	1	[b]
κ-(ET)$_2$Cu(NCS)$_2$	10.4	104	16.382	8.402	12.833	822.6	714	2	[d]
κ-(ET)$_2$Cu[N(CN)$_2$]Br	11.8	127	12.878	29.681	8.484	810.7	720	4	[e]
κ-(ET)$_2$Cu[N(CN)$_2$]Cl	12.8	127	12.909	29.658	8.418	805.7	718	4	[f]

[a] H. Yamochi, private communication.

[b] P.C.W. Leung, T.J. Emge, A.J. Schultz, M.A. Beno, K.D. Carlson, H.H. Wang, M.A. Firestone and J.M. Williams, Solid State Commun. 57 (1986) 93. For the I$_3^-$ salt, at 100 ± 30 K only the β-phase has been measured (cell parameters for average structure). For the β^*-phase, one would have to correct for effects of pressure (compressibility).

[c] U. Geiser, H.H. Wang, C.E. Hammond, M.A. Firestone, M.A. Beno, K.D. Carlson, L. Nuñez and J.M. Williams, Acta Crystallogr. C 43 (1987) 656.

[d] H. Urayama, H. Yamochi, G. Saito, S. Sato, A. Kawamoto, J. Tanaka, T. Mori, Y. Maruyama and H. Inokuchi, Chem. Lett. (1988) 463. The numbers given by Y. Watanabe, T. Sasaki, H. Sato and N. Toyota, J. Phys. Soc. Jpn. 60 (1991) 927 at 20 K are for a transformed cell (for comparison with the dicyanamide [N(CN)$_2$] salts) and represent otherwise unpublished results.
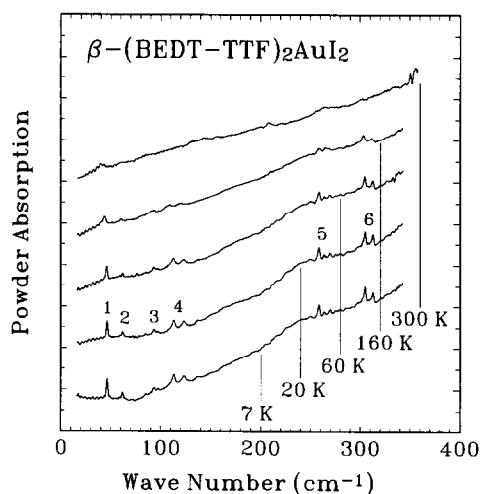
[e] Ref. [4].

[f] Ref. [6].

Fig. 5. The far-infrared powder absorption of β-(ET)$_2$AuI$_2$ at five temperatures. The resolution is 1 cm^{-1} and the spectra, displaced for clarity, are the logarithmic ratios of the transmission through a clear window to that of the transmission through the powder and window.
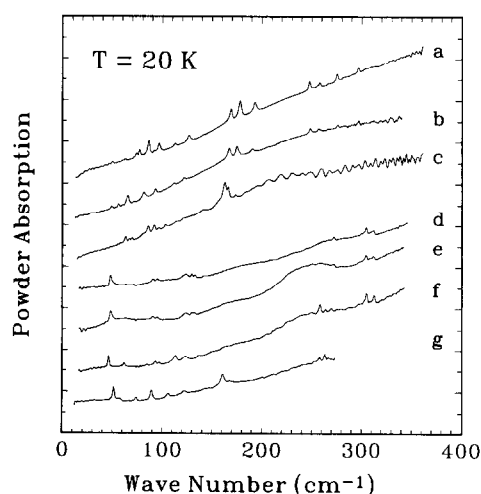

Fig. 6. The far-infrared powder absorption spectra of the seven compounds investigated in this study, displaced for clarity and arranged from bottom to top in order of increasing T_c. They are (a) κ-(ET)$_2$Cu[N(CN)$_2$]Cl, (b) κ-(ET)$_2$Cu[N(CN)$_2$]Br, (c) κ-(ET)$_2$Cu(NCS)$_2$, (d) β^*-(ET)$_2$I$_3$, (e) α_t-(ET)$_2$I$_3$, (f) β-(ET)$_2$AuI$_2$, (g) β-(ET)$_2$IBr$_2$. (See tables 1 and 5 for the values of T_c.)

top (a–c). Table 5 lists the frequencies of the features in the three β-phase and the α_t-phase compounds.

A comparison of the spectra d and e in fig. 6 as well as the last two columns in table 5 shows that the

spectra of β^*-(ET)$_2$I$_3$ and the α_t-(ET)$_2$I$_3$ are virtually identical. Along with similar values of T_c and many other physical properties, this provides a further argument that the compounds may indeed be

Table 5
The frequencies, in wavenumbers, of the powder absorption features, at 20 K, of four β or α_t phase $(ET)_2X$ salts [a]

X = $T_c =$	β-IBr_2 2.8 K	β-AuI_2 5 K	β^*-I_3 8 K at 0.5 kbar	α_t-I_3 7–8 K
1.	51.3 s	46.3 s ↓	48.2 s ↑	48.4 s
2.	73.5 w	75.0 vw ↑	71.3 vw ↓	74.0 vw
3.	89.0	92.8 w ↑	90.6 w ↓	90.6 w
	–	96.9 w	94.7 w ↓	95.2 w
4.	105.3 m	113.3 m ↑	123.9 m ↑	124.1 m
	122.0 m	123.4 m ↑	129.7 w ↑	129.9 w
	–	137.2 w	132.6 vw ↓	132.8 vw
	160.8 s	–	–	–
5.	257.7 w	258.2 s	–	–
	263.0 m	269.5 w	272.1 w	271.9 w
6.	–	304.7 s	304.2 s	304.2 m
	–	312.4 s	311.2 m	311.4 m

[a] ↑(↓) indicates an increase (decrease) in frequency compared with the column to its left. vw means very weak, w weak, m medium and s strong.

identical, and we are convinced that the Nujol mull has produced the β^*-$(ET)_2I_3$.

A comparison of the frequencies of the lattice modes (groups 1–4 in table 5) of the β-phase compounds, however, reveals mixed results. The trend towards higher T_c is not accompanied by uniformly increasing frequencies as was the case for the two κ-phase compounds. The arrows in table 5 shows a general increase in going from the IBr_2^- to the AuI_2^- salt but a mixed response in going to the I_3^- derivative. This mixed response might be due to the different enthylene group configuration in the β^*-$(ET)_2I_3$ salt compared with that in the β-$(ET)_2IBr_2$ and β-$(ET)_2AuI_2$, which are isostructural. Group 4 between 110 cm^{-1} and 130 cm^{-1} is the only group with consistently increasing frequencies as T_c increases. In so far as the frequencies of these few lattice modes are an indication of lattice stiffness, however, there appears to be little evidence for the rise

of T_c in this group of three β-phase compounds being due to lattice softness, in agreement with the κ-phase compounds. It is still possible, however, that the volume effect first noted by Williams et al. [7,8] may be operating through the increased density of states.

Two unexplained features exist in spectrum g in fig. 6, that of β-$(ET)_2IBr_2$. The first is the high wavenumber of the lowest-frequency strong feature at 51.3 cm^{-1}, when one would have expected it to be less than that of the spectrum above if a general trend were being followed. The second and more serious question is the appearance of the strong feature at 160.8 cm^{-1}, which is not present in the other two β-phase spectra, but resembles instead the group 4 of the κ-phase compounds. This latter group has an isotope shift indicating a mixture of translation and/or R_z libration. The reason that more features are seen in the κ-phase spectra than in those of the β-phase is the larger value of Z (number of formula units per

Table 6
Frequencies of the normal modes of the triatomic linear anions in the β-phase ET salts [a]. Frequencies are in cm^{-1}

(Double degenerate)	ν_1 (Raman)	ν_2 (IR) (Doubly degenerate)	ν_3 (IR)
I_3^- (solution)	114	52	145
AuI_2^- (solid)	158	67,59	210
$BrIBr^-$ (solid)	256	124	256

[a] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds (Wiley, New York, 1986).

Table 7
Values of Debye temperature, θ_D, extracted from specific heat studies

Compound	T_c	θ_D
α-$(ET)_2(NH_4)Hg(SCN)_4$	1.1 K	230 ± 10 K [a]
β-$(ET)_2I_3$	1.4 K	197 ± 5 K [b]
κ-$(ET)_2Cu(NCS)_2$	10.4 K	215 ± 10 K [c]
κ-$(ET)_2Cu[N(CN)_2]Br$	11.8 K	210 ± 15 K [d]

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unit cell; see table 4). Does the presence of the 160.8 cm^{-1} feature in spectrum g therefore indicate some disorder or modulation, which has increased the size of the unit cell? It is also possible that there is a small amount of α-$(ET)_2IBr_2$ mixed with the β-$(ET)_2IBr_2$. (The feature is not due to the anion since none of the vibrational features of the three linear anions, as listed in table 6, appear to be present with any strength in these seven powder spectra.)

Before leaving fig. 6, however, another comparison may be made. While it is not possible to compare individual features in the spectra of the κ-phase and the β-phase compounds, since the lattice modes will be different, one can observe that the overall distribution of lattice mode frequencies for the κ-phase compounds is higher than that for the β-phase. In spectrum a for example, the range is from 70 cm^{-1} to 200 cm^{-1}, while in spectrum d the features start at 50 cm^{-1} and extend to only 135 cm^{-1}. Figure 6 shows this trend quite well. Again one is led to speculate whether a suitable integral over the phonon frequencies in the prefactor of eq. (1) as considered in ref. [12] may be contributing to the increase in T_c between these compounds. It is known that inaccurate results are obtained if the Debye frequency by itself is used [12]. Furthermore, the variations of θ_D between compounds of these two phases is too small to produce the observed differences in T_c. Table 7 lists the values of θ_D extracted from specific heat measurements on various ET compounds.

What appears more likely, however, is that the equations (1–4) are inappropriate for these materials. Recent muon-spin-relaxation measurements [24] by Le et al. indicate non-BCS-type s wave pairing, and instead anisotropic pairing with line nodes in the energy gap. This would agree with our null result when we tried to observe the energy gap optically [25]. On a plot of T_c versus Fermi temperature, the organic salts, heavy fermion materials, and high-T_c cuprates all sit on the same straight line, far apart from the BCS-type metals [26].

4. Conclusion

We have measured the frequencies of some of the infrared-active lattice vibrations at various temperatures of three κ-phase and three β-phase organic superconductors based on the BEDT-TTF donor molecule. We found a general increase in these frequencies as T_c increases in the κ-phase compounds, consistent with the decreasing volume of the unit cell. We found a mixture of increases and decreases in the frequencies of the β-phase compounds as T_c increases, consistent with the combination of an increasing volume of the unit cell together with a decrease in one of the lattice constants. In general, the observed frequencies of the higher-T_c κ-phase compounds are higher than those of the β-phase materials, although a strict comparison is not possible. We find no evidence that higher values of T_c in these materials are achieved through a softer lattice. On the contrary, it is possible that the higher optical-phonon frequencies may be contributing to the increase in T_c, but it is likely to be a much more complicated situation than that described by a simple BCS expression.

Acknowledgements

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