

Lattice Dynamics of Fullerenes Probed by Organometallic Intercalates<sup>†</sup>

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The 14.4 keV nuclear  $\gamma$ -ray resonance in  $^{57}\text{Fe}$  has been used as a probe of the hyperfine interactions and lattice dynamics of the bisferrocene (Fc) intercalates of  $\text{C}_{60}$  and  $\text{C}_{70}$ . Over the temperature range  $90 \leq T \leq 350$  K the isomer shift is a smooth function of  $T$  and is very similar for neat Fc and the two intercalates. In contrast, the  $T$ -dependence of the quadrupole hyperfine interaction undergoes a marked change in slope at  $\sim 300$  K in  $\text{C}_{60}\text{Fc}_2$ , but not in  $\text{C}_{70}\text{Fc}_2$ . A similar discontinuity at  $\sim 300$  K is observed in the temperature dependence of the recoil-free fraction in  $\text{C}_{60}\text{Fc}_2$ , but not in  $\text{C}_{70}\text{Fc}_2$ . These observations can be related to the known phase change and onset of fullerene rotation in the former (as contrasted to the latter) and are supported by DSC measurements in the interval  $240 \leq T \leq 380$  K for both intercalates.

## Introduction

Although the incorporation of *endohedral* metal atoms which can be subjected to temperature-dependent Mossbauer effect studies of fullerenes is still beyond experimental reach, the use of such methods employing *exohedral* metal containing species has been reported in several earlier studies.<sup>1</sup> In the case of  $\text{C}_{60}\text{-Fe}(\text{CO})_4$ , persuasive evidence was cited<sup>2</sup> for the formation of a relatively strong covalent  $\sigma$ -bond between the metal center and the carbon structure. However, due to the instability of this compound above about 240 K, no conclusions related to the lattice dynamics of the  $\text{C}_{60}$  structure near room temperature could be extracted from the available data.

The reported preparation of a ferrocene intercalate of  $\text{C}_{60}$  by Crane et al.<sup>3</sup> opened up the possibility of using the Mossbauer resonance of  $^{57}\text{Fe}$  of the organometallic guest to probe the lattice dynamics of the fullerene in a matrix where the host–guest interaction was relatively weak. A Mossbauer study of a presumed ferrocene intercalate of  $\text{C}_{60}$  has been reported by Kucharski et al.<sup>4,5</sup> over the temperature range  $78 \leq T \leq 300$  K, but the chemical identity of the system examined by them is open to some question. A more recent study of a well-characterized  $\text{C}_{60}\text{Fc}_2$  system over the temperature range  $80 < T < 300$  K confirms that the chemical interaction between the fullerene and ferrocene is very weak.<sup>6</sup> Since the lattice dynamics and hyperfine interactions of both *neat* ferrocene and ring-substituted ferrocenes have recently been reported in some detail,<sup>7,8</sup> it was considered worthwhile to extend the examination of the  $\text{C}_{60}$  ferrocene system,  $\text{C}_{60}\text{Fc}_2$ , as well as of the related  $\text{C}_{70}\text{Fc}_2$ , to somewhat higher temperatures, and the present investigation reports the results of such a study over the temperature range  $90 < T < 375$  K.

## Experimental Section

**(a) Synthesis and Structure Verification.** Commercially obtained ferrocene was slowly recrystallized from acetone, and the resultant large single crystals were reduced to microcrystallite size by grinding in the presence of a small amount of Pyrex glass powder. The  $\text{C}_{60}\text{Fc}_2$  sample was prepared using the method described by Crane et al.<sup>3</sup> The  $\text{C}_{70}\text{Fc}_2$  was prepared by combining benzene or carbon disulfide solutions of  $\text{C}_{70}$  and ferrocene in a 2:1 volume ratio. After about 10 days the resulting microcrystalline solid was collected by decantation and dried, and excess ferrocene was sublimed from the dark solid at  $T < 80$  °C under vacuum, providing the pure  $\text{C}_{70}\text{Fc}_2$ . The phase purity of both the  $\text{C}_{60}\text{Fc}_2$  and  $\text{C}_{70}\text{Fc}_2$  was confirmed by powder X-ray diffraction studies using a Siemens D5000 diffractometer. The structure of the microcrystalline  $\text{C}_{70}\text{Fc}_2$  sample was confirmed by comparison with the single-crystal X-ray diffraction data of  $\text{C}_{70}\text{Fc}_2$  reported by Balch et al.<sup>9</sup>

**(b)  $^{57}\text{Fe}$  Mossbauer Spectroscopy.** The experimental samples, ferrocene (Fc),  $\text{C}_{60}\text{Fc}_2$ , and  $\text{C}_{70}\text{Fc}_2$ , were dispersed in BN to effect random crystallite orientation and were mounted in plastic sample holders in a normal transmission geometry Mossbauer spectrometer, as described earlier.<sup>7,8</sup> The samples were optically “thin” (involving ca.  $3 \times 10^{17}$   $^{57}\text{Fe}$  atoms  $\text{cm}^{-2}$ ) and thus were treated in the subsequent data analysis without saturation corrections. The Mossbauer source used was  $\sim 10$  mCi  $^{57}\text{Co}$  in a Rh matrix. In general, spectra having in excess of  $10^6$  counts per channel were collected at each temperature, which itself was monitored continuously with a compensated thermocouple over the data acquisition period. Spectrometer calibration was effected using a standard 18.8 mg  $\text{cm}^{-2}$  alpha iron absorber, and all isomer shifts are reported with respect to the centroid of a room-temperature spectrum of this absorber. Data reduction was effected using a matrix inversion least-squares fitting program, in which line position, line width, effect magnitude, and baseline nonlinearity were each allowed to vary as free parameters.

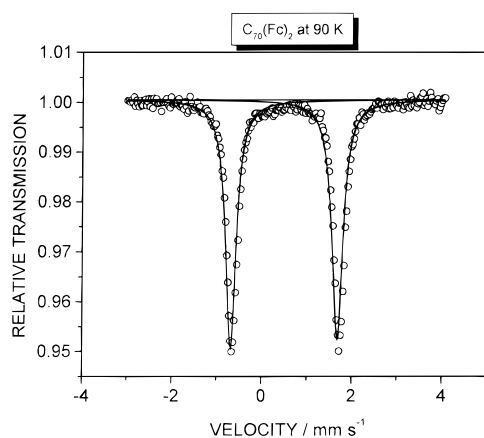
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<sup>†</sup> Dedicated to the memory of Sir Geoffrey Wilkinson, NL, FRS.

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TABLE 1

parameter	ferrocene (Fc)	C <sub>60</sub> Fc <sub>2</sub>	C <sub>70</sub> Fc <sub>2</sub>
IS (90), mm s <sup>-1</sup>	0.530 ± 0.003	0.530	0.531
IS (300), mm s <sup>-1</sup>	0.458	0.441	0.447
QS, mm s <sup>-1</sup>	2.428 ± 0.023 (85 < T < 300)	2.390 ± 0.026 (90 < T < 297)	2.384 ± 0.006
-d IS/dT × 10 <sup>4</sup> , mm s <sup>-1</sup> K <sup>-1</sup>	3.83 ± 0.10	4.22 ± 0.12	2.76 (86 < T < 170) 4.88 (170 < T < 375)
-d lnA/dT × 10 <sup>3</sup> K <sup>-1</sup>	8.66 ± 0.73	4.95 ± (90 < T < 270) 11.74 ± 0.14 (280 < T < 350)	2.94 ± 0.04 (85 < T < 170) 6.23 ± 0.03 (170 < T < 375)
Θ <sub>M</sub> , K	91 ± 4	130 (90 < T < 270) 82 (280 < T < 350)	
M <sub>eff</sub> , Da	109 ± 2	99	150 (85 < T < 170) 85 (170 < T < 375)



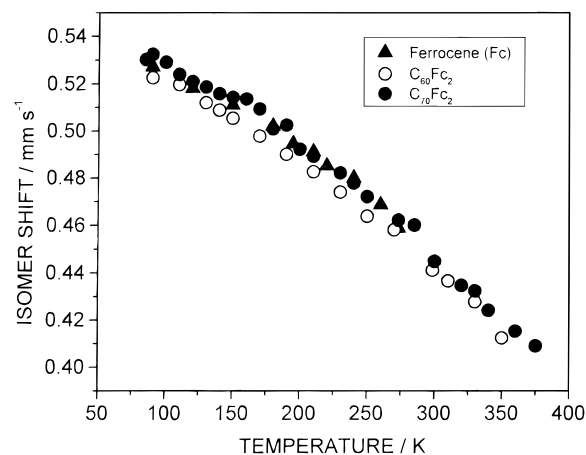
**Figure 1.** <sup>57</sup>Fe Mossbauer spectrum of C<sub>70</sub>Fc<sub>2</sub> at 90 K. The velocity scale is with reference to a room-temperature spectrum of α-Fe.

(c) **Differential Scanning Calorimetry.** Samples of the subject materials were examined by programmed variable temperature techniques using both Perkin-Elmer DSC-7 and Mettler Model DSC30 instruments at scanning rates of 4–6 deg/min. Baseline corrections were applied as needed to the raw experimental data.

## Results and Discussion

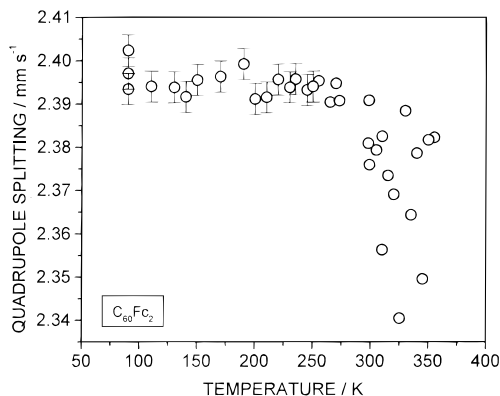
**C<sub>60</sub>Fc<sub>2</sub>.** As expected, the <sup>57</sup>Fe Mossbauer parameters at 90 K of C<sub>60</sub>Fc<sub>2</sub> and C<sub>70</sub>Fc<sub>2</sub> are very similar to those of neat ferrocene, and the appropriate numerical values are summarized in Table 1. Moreover, the low-temperature (90 ≤ T ≤ 297 K) data for C<sub>60</sub>Fc<sub>2</sub> are in good agreement with the values reported by Vertes et al.<sup>6</sup> but depart from these values in the high-temperature regime. The spectra consist of a single quadrupole-split doublet, having line widths of 0.26–0.28 mm s<sup>-1</sup> (uncorrected) over the entire temperature range. A typical spectrum is shown in Figure 1.

The Mossbauer parameters of single-crystal ferrocene have been reported in detail by Gibb,<sup>10</sup> and this work has recently been extended to related systems involving ring-substituted complexes.<sup>7</sup> It should be noted, however, in the following discussion, that in contrast to neat ferrocene, in which the two cyclopentadienyl rings (at low temperatures) are staggered,<sup>11</sup> in C<sub>60</sub>Fc<sub>2</sub>—as pointed out by Crane et al.<sup>3</sup> (and C<sub>70</sub>Fc<sub>2</sub>)—the rings are eclipsed. Moreover, within any one single crystal of C<sub>60</sub>Fc<sub>2</sub> and C<sub>70</sub>Fc<sub>2</sub>, all ring planes are parallel. In this context, it should be pointed out that in contrast to the data interpretation by Vertes et al.<sup>6</sup> there is no persuasive evidence in the present data for a significant Gol'danskii–Karyagin asymmetry in the spectral data over the range 90 ≤ T ≤ 300 K for both C<sub>60</sub>Fc<sub>2</sub> and C<sub>70</sub>Fc<sub>2</sub>. Due to the small recoil-free fraction values above 300 K, the suggestion of a small T-dependent area asymmetry has not been pursued in detail in the present study.

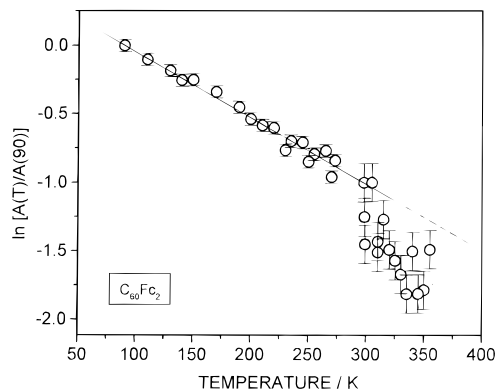


**Figure 2.** Temperature dependence of the isomer shift parameter for neat ferrocene (solid triangles) and the ferrocene intercalates of C<sub>60</sub> (open circles) and C<sub>70</sub> (solid circles). This figure is meant to illustrate the qualitative similarity in the three data sets (see, also, Figure 6).

The temperature dependence of the isomer shift (d IS/dT) for a neat, microcrystalline, sample of ferrocene shows some departure from linearity in the higher temperature regime. This nonlinearity is a generally observed phenomenon in covalent solids and has been noted previously.<sup>7,8</sup> The exact nature of this nonlinear decrease in IS with increasing T is not clearly established,<sup>12</sup> but a major contributing effect is presumably due to the normal thermal expansion of organometallic (predominantly covalent) solids. The observed data are in good agreement with the single-crystal data of Gibb<sup>10</sup> and, despite the above caveat, are reasonably well fitted by a linear regression. The slope corresponds to  $(3.828 \pm 0.085) \times 10^{-3}$  mm s<sup>-1</sup> K<sup>-1</sup> over the range 90 ≤ T ≤ 300 K. The “effective vibrating mass” (M<sub>eff</sub>)<sup>13</sup> value calculated from these data is 109 ± 2 Da. For C<sub>60</sub>Fc<sub>2</sub>, the IS parameter is also reasonably well fit by a linear regression over the range 90 ≤ T ≤ 350 K (although there is some curvature evident in the data), as summarized in Figure 2, and its temperature dependence is  $(4.216 \pm 0.004) \times 10^{-3}$  mm s<sup>-1</sup> K<sup>-1</sup>. The corresponding M<sub>eff</sub> value is 99 Da. The temperature dependence of IS for C<sub>70</sub>Fc<sub>2</sub> shows a somewhat different behavior and will be considered more fully below. As has been repeatedly noted in the literature,<sup>14</sup> the quadrupole interaction parameter (QS) in ferrocene and related complexes is insensitive to ring substitution and is not expected to be significantly different in the examined systems. In all three cases (ferrocene, C<sub>60</sub>Fc<sub>2</sub>, and C<sub>70</sub>Fc<sub>2</sub>) over the indicated low-temperature range(s), the QS can be treated as a T-independent parameter within the experimental errors quoted and is very similar in all three instances; the corresponding values are included in Table 1 and require no further comment. The very small negative temperature dependence of d QS/dT, evident in the data of Kucharski et al.,<sup>5</sup> is also seen



**Figure 3.** Temperature dependence of the quadrupole splitting parameter for  $C_{60}Fc_2$ . The error bars in the range  $90 \leq T \leq 250$  K are extracted from a linear least-squares fit to the data and give some idea of the precision of the data.

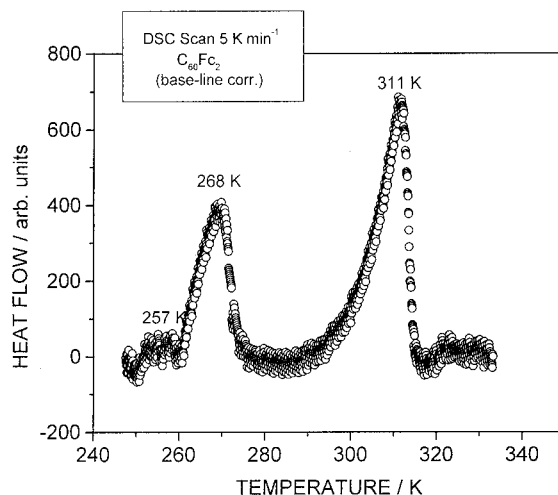


**Figure 4.** Temperature dependence of the logarithm of the area under the resonance curve for  $C_{60}Fc_2$ .

in the present study (but not deemed significant with respect to the experimental error limits shown in Table 1), and it has been possible to confirm the significant decrease in QS at  $T > \sim 275$  K reported by them, as is evident from the data summarized in Figure 3.

The temperature dependence of the recoil-free fraction, taken as the temperature dependence of the area under the resonance curve for a "thin" absorber, is summarized graphically in Figure 4, from which the change in slope of  $\ln A$  at  $T \approx 275$  K is clearly evident. The  $T$ -dependence in the range  $90 \leq T \leq 270$  K is well fitted by a linear regression, with a slope of  $-4.954 \times 10^{-3} \text{ K}^{-1}$ . Above 270 K, the corresponding slope is  $\sim 11.7 \times 10^{-3}$ , indicating a considerable increase in the mean square amplitude of vibration of the probe Fe atom above the inflection point. It is interesting to note (Table 1) that the ferrocene "guest" molecule appears to be held more tightly in the  $C_{60}$  "host" matrix below 270 K than it is in neat ferrocene, while the converse is true above this temperature. The  $\ln A(T)$  and IS( $T$ ) data permit a calculation of the Mossbauer lattice temperature,  $\Theta_M$ . The value reported earlier<sup>7</sup> for neat ferrocene is  $91 \pm 4$  K; the corresponding values for  $C_{60}Fc_2$  in the low- and high-temperature regime are 130 and 82 K, respectively. The former is considerably lower than the value of 151 K cited for  $C_{60}Fc_2$  in one of the earlier studies<sup>5</sup> and should be compared to the low- $T$ -regime result of Vertes et al.<sup>6</sup> (115.7 K). Indeed, it is interesting to note that the data cited in ref 6 suggests a change in the slope ( $-d \ln A/dT$ ) at the highest temperature reported by them.

These results appear to be consistent with—and supported by—the DSC scan of  $C_{60}Fc_2$  shown in Figure 5. This scan (which has been baseline corrected to educe the relatively small

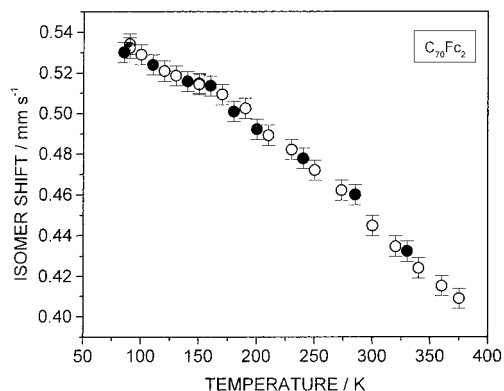


**Figure 5.** Differential scanning calorimeter data for  $C_{60}Fc_2$ . The data have been baseline corrected and are shown in arbitrary units (ordinate).

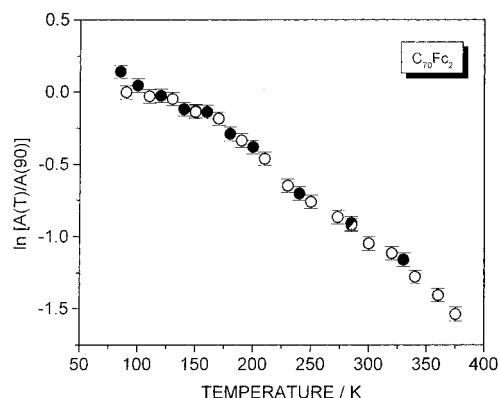
signal from a constantly varying "background") shows two relatively broad endotherms, having maxima at  $\sim 268$  and 311 K. These endotherms can be understood in terms of the corresponding data reported by Yang et al.<sup>15</sup> for the parent fullerene, which evidenced two such maxima at 251.4–259.9 and 270–310 K. Yang et al.<sup>15</sup> ascribe these two endotherms to a lattice transition from simple cubic to fcc (orientational order with onset of fullerene rotation) at the lower temperature and random orientation and rapid  $C_{60}$  rotation at the higher temperature. Heiney et al.<sup>16</sup> report a single DSC peak at  $\sim 261$  K, while Dworkin et al.<sup>17</sup> report an exothermic peak on cooling starting at 257.2 K, while an endothermic peak is observed on heating at 257.1 K. Similar interpretations of synchrotron radiation powder diffraction patterns in terms of an order–disorder transition have been reported by Heiney et al.,<sup>16</sup> who place this discontinuity at about 249 K, while Moret,<sup>18</sup> using similar experimental techniques, reports a value of  $\sim 259$  K. In addition, a number of related studies<sup>19,20</sup> of the order–disorder transition in  $C_{60}$  have shown that the 259 K transformation is observed at a considerably higher temperature (325 K) in  $C_{60}K_{1.3}$ . Thus in the ferrocene intercalate, it appears that the lower temperature phase transition is shifted upward by about 10–15 K from the value observed for neat  $C_{60}$ . The onset of rapid  $C_{60}$  rotation weakens the ferrocene– $C_{60}$  interaction (as reflected in the recoil-free fraction data) and causes a noticeable change in the quadrupole interaction of the nearly free (and isolated) ferrocene guest molecule.

**$C_{70}Fc_2$ .** Turning next to  $C_{70}Fc_2$ , the  $^{57}\text{Fe}$  Mossbauer data parallel (with some significant exceptions) the data for the  $C_{60}$  homologue summarized above. Both the isomer shift at low temperatures and its temperature dependence are almost indistinguishable from those of neat ferrocene and the  $C_{60}Fc_2$  intercalate, as reflected in Figure 2, except that there appears to be a distinct change in slope at about 170 K, as shown more clearly in Figure 6. Above this temperature (to 360 K), the temperature dependence of IS is a factor of 1.7 larger than the low-temperature value. The  $M_{\text{eff}}$  value calculated from the data in the 85–170 K interval is 150 Da, significantly larger than the values calculated for ferrocene and the  $C_{60}Fc_2$  system, while this parameter drops to 85 Da for the higher temperature regime.

As noted above, the QS parameter is nearly temperature independent (mean value over the range  $85 \leq T \leq 375$  K is  $2.384 \pm 0.006 \text{ mm s}^{-1}$ ) with a slope of  $-(2.68 \pm 1.22) \times 10^{-5} \text{ mm s}^{-1} \text{ K}^{-1}$ . In contrast to the  $C_{60}$  homologue, there is no evidence for a distinct change in the  $T$ -dependence of this parameter at  $\sim 300$  K.



**Figure 6.** Temperature dependence of the isomer shift parameter for  $C_{70}Fc_2$ . This figure is meant to show the change in slope at  $T \approx 170$  K, as discussed in the text.



**Figure 7.** Temperature dependence of the logarithm of the area under the resonance curve for  $C_{70}Fc_2$ . The open circles represent data acquired on sequentially heating the sample from 90 K; the closed circles represent the corresponding cooling cycle data, reflecting the reversibility of the dynamic phenomena discussed in the text.

The temperature dependence of the recoil-free fraction is summarized graphically in Figure 7 and must be considered in consonance with the known phase transitions in the  $C_{70}$  host lattice. The phase transitions and ordering in  $C_{70}$  have been discussed by Vaughan et al.,<sup>21</sup> who conclude that above 345 K the solid can be considered as a plastic crystal with an fcc structure. At lower temperatures ( $295 \leq T \leq 345$  K), orientational freezing occurs in two stages, with disorder persisting about the long axis of the molecule while the lattice undergoes a rhombohedral distortion. Below 295 K, the rhombohedral distortion undergoes a further distortion, resulting in monoclinic structure (static). The rhombohedral and fcc structures coexist to at least 200 K. At lower temperatures, a lower symmetry phase (monoclinic) is present. At all temperatures,  $C_{70}$  retains the ABC packing sequence. A DSC scan<sup>22</sup> of the neat fullerene shows two (broad) endotherms, with onsets at  $\sim 280$  and  $\sim 330$  K (maxima at  $\sim 300$  and  $\sim 360$  K). In contrast, a DSC scan of  $C_{70}Fc_2$  shows no evidence for the kind of endothermic phase transitions noted for  $C_{60}Fc_2$ , above, and the heat-flow profile is that of a featureless gradual change in the interval  $240 \leq T \leq 380$  K. In this context, it is interesting to note that the  $^{57}\text{Fe}$  Mossbauer data for the ferrocene intercalate, in the regime below  $T \approx 270$  K, parallel those for the  $C_{60}$  homologue quite closely, and the slope is significantly shallower than that observed for neat ferrocene, suggesting a smaller mean square amplitude of vibration of the iron atom in the fullerene intercalate than in the parent organometallic. It should be noted, however, that there is no evidence for the change in slope noted

at  $T \approx 300$  K (see Figure 4) for the  $C_{60}$  system. Since this inflection point can presumably be associated with the onset of rapid rotation of the  $C_{60}$  moiety (vide supra) in the former, its absence in the latter suggests that the departure from spherical symmetry in  $C_{70}$  pushes the onset of this rotation to a significantly higher temperature.

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