

Solid State Dynamics of  $\text{Fe}_3(\text{CO})_{12}$  Revisited

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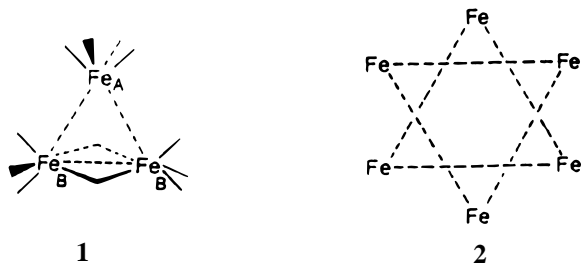
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Nature has indeed been kind in providing three simple but, for different reasons, fascinating iron carbonyl complexes, namely  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}_2(\text{CO})_9$ , and  $\text{Fe}_3(\text{CO})_{12}$ . Perhaps the most intriguing of these compounds is  $\text{Fe}_3(\text{CO})_{12}$ , **1**, a compound which has a long history<sup>1</sup> dating back to the original Star of David structure, **2**, proposed by Dahl and Blount<sup>2</sup> and subsequently confirmed by single-crystal X-ray structural studies<sup>3,4</sup> and extensive related work.<sup>5–7</sup>



Although in solution  $\text{Fe}_3(\text{CO})_{12}$  is very flexible, such that the carbonyl groups remain equivalent down to 123 K, the situation is very different in the solid state. The Star of David disordered structure, **2**, results because  $\text{Fe}_3(\text{CO})_{12}$  is located on an inversion center, as a consequence of the spacial average of the molecules in two antisymmetric orientations each of which is, on average, 50% occupied throughout the crystal. This disorder could result from either (1) a static orientation of the three iron atoms in two centrosymmetric locations in the icosahedral like cage formed by the carbonyl ligands, an icosahedral cage which is itself invariant upon inversion, (2) a composite disordered macrostructure of twinned ordered cells,<sup>8</sup> or (3) a dynamic reorientational relaxation by  $60^\circ$  of the three iron atoms within the icosahedral cage. The last dynamic reorientational model has been proposed<sup>9</sup> as consistent with the solid state magic angle spinning carbon-13 NMR spectra of  $\text{Fe}_3(\text{CO})_{12}$ .

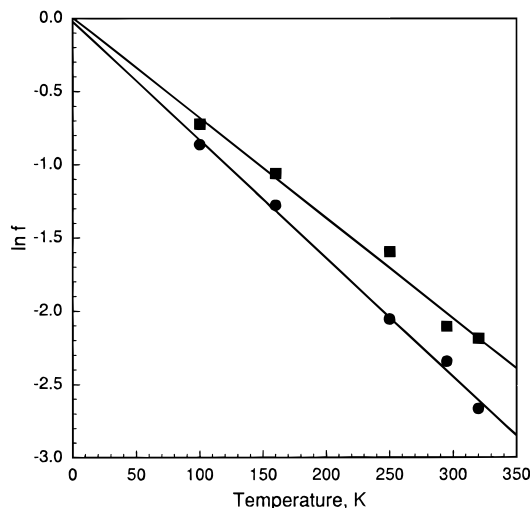
Several years ago we reported<sup>6</sup> a detailed study of the temperature dependence of the Mössbauer spectra of  $\text{Fe}_3(\text{CO})_{12}$  with the goal of distinguishing between the above mentioned static and dynamic structural models, at least on the Mössbauer

time scale of  $10^{-8}$  s. From a careful analysis of the spectral line shape as a function of temperature, we found that it was *not* possible to show that, with any reasonable relaxation model,  $\text{Fe}_3(\text{CO})_{12}$  was undergoing, on this time scale, any relaxation by  $60^\circ$  rotations. However, the temperature dependence of the Mössbauer spectra did reveal two unusual aspects of the structural dynamics of  $\text{Fe}_3(\text{CO})_{12}$ . Because the ratio of the area of the outer quadrupole doublet, assigned to  $\text{Fe}_B$ , to that of the inner doublet, assigned to  $\text{Fe}_A$ , decreased from 1.9 at 4.2 K to 1.27 at 300 K, we concluded that the recoil-free fractions,  $f_A$  and  $f_B$ , for the two sites must be different and have different temperature dependences. Equal or similar recoil-free fractions with similar temperature dependences would lead to a ratio of ca. 2 which is independent of temperature. Indeed the values of the recoil-free fractions obtained at 300 K were different for the two sites and agreed almost exactly with those obtained from the thermal parameters reported by Cotton and Troup.<sup>4</sup> In addition, the asymmetry in the area of the two lines composing the outer quadrupole doublet assigned to  $\text{Fe}_B$  could only be understood as arising from the Goldanskii–Karyagin effect, an effect which results from an anisotropy in the thermal vibration of the iron atoms. Once again, the asymmetry observed in the outer doublet at 300 K agreed virtually perfectly with that predicted from the anisotropy in the thermal parameters reported by Cotton and Troup.<sup>4</sup> It is very unusual and difficult to observe the Goldanskii–Karyagin effect in an iron-57 Mössbauer spectrum, and  $\text{Fe}_3(\text{CO})_{12}$  represents only the second documented compound to display this effect with iron-57, the first being  $\text{FePS}_3$ .<sup>10</sup> One of the reasons it is possible to observe the Goldanskii–Karyagin effect<sup>11</sup> in  $\text{Fe}_3(\text{CO})_{12}$  is that the recoil-free fractions are very small,<sup>6</sup> ca. 0.1, in this compound.

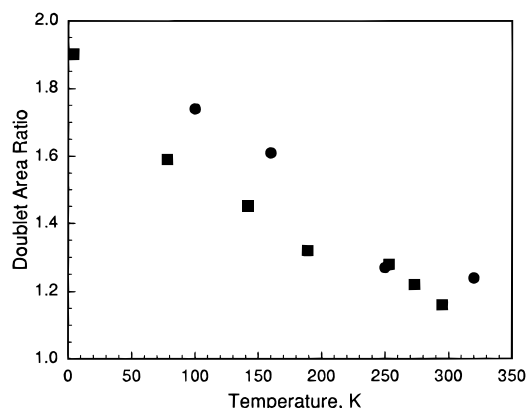
More recently, Braga et al.<sup>7</sup> studied the temperature dependence of the X-ray structure of  $\text{Fe}_3(\text{CO})_{12}$  between 100 and 320 K with the goal of elucidating its structural dynamics. In agreement with our earlier conclusion,<sup>6</sup> they found no evidence for the  $60^\circ$  rotational relaxation mentioned above, presumably because, if it occurs, it is slow<sup>9</sup> on the X-ray time scale, but rather they found an increasingly anisotropic vibration for the  $\text{Fe}_B$  sites, a vibration which has a large amplitude normal to the plane of the three iron atoms. From their reported thermal parameters it is possible to calculate<sup>12</sup> the equivalent recoil-free fractions for the two iron sites in  $\text{Fe}_3(\text{CO})_{12}$ . The results of these calculations are shown in Figure 1 and clearly show, in agreement with the predictions from our Mössbauer spectral work, that  $f_A > f_B$  and that the temperature dependence is different for the two sites. The Debye temperatures deduced

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**Figure 1.** Temperature dependence of the logarithm of the recoil-free fractions calculated from the vibrational amplitudes measured by Braga et al.<sup>7</sup> for Fe<sub>A</sub> (■) and Fe<sub>B</sub> (●) in Fe<sub>3</sub>(CO)<sub>12</sub>.

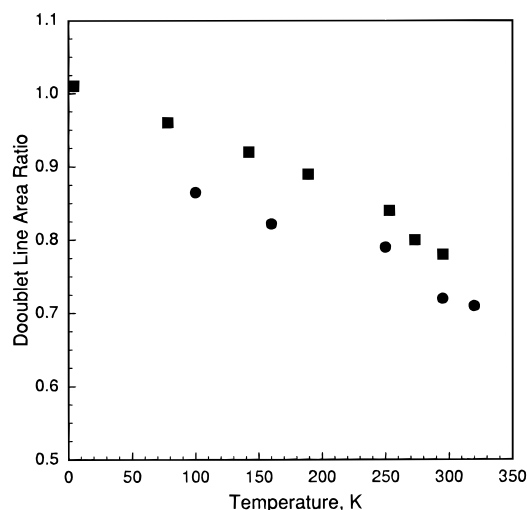


**Figure 2.** Temperature dependence of the experimental<sup>6</sup> (■) and calculated<sup>7</sup> (●) doublet area ratio in the Mössbauer spectrum of Fe<sub>3</sub>(CO)<sub>12</sub>. Equivalent recoil-free fractions for the two sites would yield temperature-independent values of 2.00.

from the slopes of the straight lines in Figure 1 are 182 and 187 K, for the A and B sites, respectively.

The temperature dependence of the area ratio of the two quadrupole doublets, as observed<sup>6</sup> in the Mössbauer spectra and as predicted on the basis of the X-ray thermal parameters,<sup>7</sup> is shown in Figure 2. Although the temperature dependences are not exactly the same, the agreement is good, especially considering the very different sources of the experimental results. The X-ray measurements of Braga et al.<sup>7</sup> have shown that the vibrational anisotropy is not completely frozen out at 100 K, in agreement with the Mössbauer spectral results obtained<sup>6</sup> at 78 and 142 K. Furthermore, the area ratio of 1.9 measured in the 4.2 K Mössbauer spectrum (Figure 2) indicates that the anisotropic vibrational motion of the iron atoms normal to the plane of the molecule is still present even at 4.2 K.

As indicated above, the Goldanskii–Karyagin<sup>11</sup> asymmetry expected in a Mössbauer spectrum may be predicted from the anisotropy in the thermal parameters. The temperature dependence of the anisotropy in these parameters has been nicely



**Figure 3.** Temperature dependence of the experimental<sup>6</sup> (■) and calculated<sup>7</sup> (●) outer doublet line area ratios in the Mössbauer spectrum of Fe<sub>3</sub>(CO)<sub>12</sub>. In the absence of the Goldanskii–Karyagin effect the value would be 1.00 and independent of temperature.

illustrated by Braga et al.,<sup>7</sup> who find that the major axes of the thermal ellipsoids for the Fe<sub>B</sub> sites are normal to the plane of the molecule. We have used their thermal parameters to calculate<sup>12</sup> the Goldanskii–Karyagin asymmetry, i.e., the area ratio of the two components of the outer quadrupole doublet. As shown in Figure 3, there is excellent agreement between the observed asymmetry and that calculated from the thermal anisotropy. Indeed this provides solid support for our earlier,<sup>6</sup> and in part controversial,<sup>13</sup> finding of the Goldanskii–Karyagin effect in this compound.

In conclusion, the recent X-ray measurements by Braga et al.<sup>7</sup> on Fe<sub>3</sub>(CO)<sub>12</sub> between 100 and 320 K have allowed us to extend the analysis of our previous Mössbauer spectral measurements,<sup>6</sup> in terms of the anisotropic vibration of the carbonyl-bridged iron atoms, to temperatures below 300 K. Between 100 and 320 K, there is excellent agreement between the temperature dependences of the calculated and experimental values of the doublet area ratio (see Figure 2). Furthermore, there is also excellent agreement between the calculated and experimental values of the line area ratio and its temperature dependence for the doublet assigned to the carbonyl-bridged iron atoms. Hence, the anisotropic vibration that we first proposed,<sup>6</sup> and that has now been confirmed by Braga et al.,<sup>7</sup> is completely consistent with the temperature dependences of the two recoil-free fractions in Fe<sub>3</sub>(CO)<sub>12</sub>, completely supports the somewhat controversial<sup>13</sup> observation of the Goldanskii–Karyagin asymmetry in this compound, and eliminates the possibility of the 60° rotational disorder, at least on the Mössbauer time scale.

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