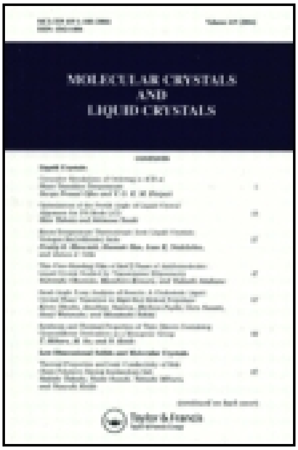

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^{129}I-Mössbauer and X-Ray Diffraction Studies of the Iodine-Fullerene Compound $C_{60}(I_2)_{-2}$

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^{129}I-MÖSSBAUER AND X-RAY DIFFRACTION STUDIES OF THE IODINE-FULLERENE COMPOUND $C_{60}(I_2)_{\sim 2}$

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Abstract: *^{129}I-Mössbauer spectroscopy was applied to study the chemical nature of iodine in $C_{60}(I_2)_{\sim 2}$. Spectra in the temperature region 4.2 K - 120 K reveal the presence of two inequivalent sites of iodine with hyperfine parameters related to those of molecular iodine. The two sites have different local symmetry and different anisotropic binding strength. These findings are discussed in conjunction with a recent x-ray diffraction study of single-crystalline $C_{60}(I_2)_{\sim 2}$ yielding also two inequivalent iodine sites with drastically different vibrational amplitudes. The synopsis of the informations obtained from both studies reveals a detailed structural model for the arrangement of the inserted I_2 molecules in the hexagonal lattice of $C_{60}(I_2)_{\sim 2}$.*

INTRODUCTION

After the preparation of subgramm quantities of the C_{60} molecule [1] intensive studies of this material resulted in the discovery of metallic and superconducting phases of charge-transfer (CT) systems with donors such as alkali and alkaline-earth metals [2]. Comparison of ionization potentials of C_{60} [3] and some aromatic hydrocarbons gave some hope for the existence of C_{60} CT-complexes with electron acceptors. Speculations about possible superconductivity in iodinated C_{60} [4] were followed by a series of publications reporting that the reaction of C_{60} with iodine vapor yields dielectric non-stoichiometric compounds with a chemical formula $C_{60}I_{\sim 4}$ [5-8]. From x-ray diffraction (XRD) data [5] a hexagonal sheet structure resembling that of graphite intercalation compounds (GIC) was derived. In this structure the C_{60} molecules form a simple hexagonal lattice, while iodine molecules are distributed in the large interstices in a rather disordered fashion [5]. There remained some open questions about the location and properties of the inserted iodine molecules in this structure. An x-ray absorption study, for instance, determined an intramolecular $d_{I\text{-}I}$ distance of 2.78 Å, markedly larger than the value 2.52 Å derived in the above structure determination [5]. A variety of other studies [6-9], however, agreed in the main conclusion that iodine in $C_{60}(I_2)_{\sim 2}$ is in molecular form and that there is no significant C_{60}-iodine charge transfer.

Here we present the results of a ^{129}I-Mössbauer study of $C_{60}(I_2)_{\sim 2}$ and discuss the results in conjunction with a recent XRD study of a single crystal of $C_{60}(I_2)_{\sim 2}$ giving more detailed informations about the location of iodine in the hexagonal C_{60} lattice including vibrational amplitudes. The synopsis of both studies reveals a detailed structural model of the intercalated I_2 molecules.

SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The sample used for the Mössbauer studies was prepared by gas-phase reaction of C_{60} and elemental iodine in an evacuated silica glass ampoule at 560 K and subsequent slow cooling. Elemental analysis yielded a composition of $C_{60}I_{3.64(4)}$. XRD spectra reveal the phase-pure hexagonal structure observed in previous studies [5-7]. Further information about the sample preparation and experimental details about the 27.7 keV (7/2 - 5/2) Mössbauer resonance may be found in Ref. 9, where also a preliminary report on the present Mössbauer data is given.

MÖSSBAUER RESULTS

Figure 1 shows Mössbauer spectra of $C_{60}I_{3.64}$ at various temperatures. The spectra are composed of two subspectra with different values of the isomer shift S and the electric-quadrupole interaction tensor (defined by the main component, $\nu_Q = eQV_{zz}/h$, and the asymmetry parameter, $\eta = (V_{xx} - V_{yy})/V_{zz}$), where V_{ii} are the components of the electric-field gradient tensor with the convention that $|V_{xx}| < |V_{yy}| < |V_{zz}|$). The fitted parameters are listed in Tab. 1 together with data of molecular iodine as reference system. The isomer shift of site 1 is by 0.22 mm/s more positive, and that of site 2 by 0.31 mm/s more negative when compared with molecular iodine. Subspectrum 1 exhibits an axially-symmetric quadrupole splitting, which is ~18% larger than that in molecular I_2, while subspectrum 2 exhibits a quadrupole splitting which is ~16% smaller than in molecular I_2 with a considerable asymmetry parameter ($\eta = 0.31$). The relative intensities of the two sites change drastically with temperature. While the relative intensity of subspectrum 1 and 2 is 1 : 0.73 at 4.2 K, it decreases to 1 : 0.11(1) at 120 K. The

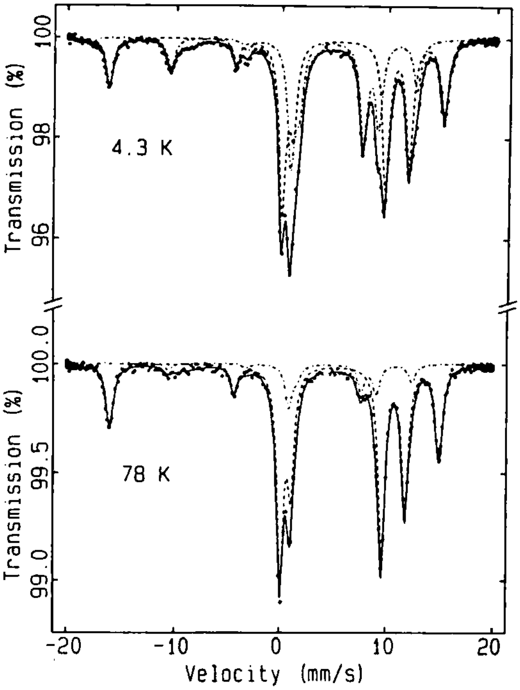

Fig. 1: ^{129}I-Mössbauer spectra of $C_{60}I_{3.64}$ at different temperatures. Subspectrum 1 (2) is plotted by dashed (dashed-dotted) lines.

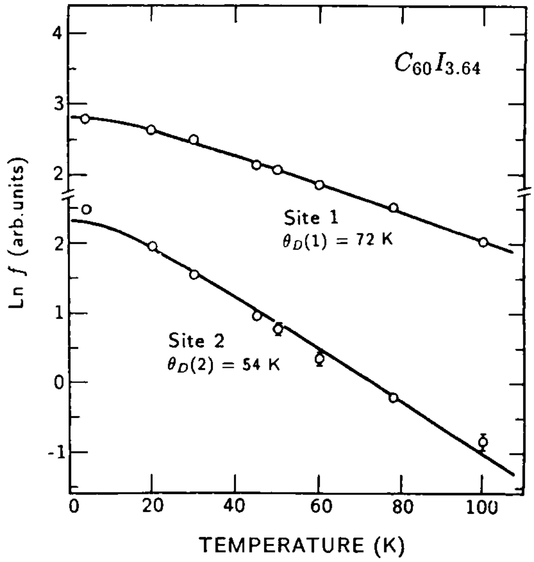

Fig. 2: Temperature dependence of the spectral areas (Mössbauer Debye-Waller factors or f-factors) of the site 1 and site 2 in $C_{60}I_{3.64}$. The solid lines are Debye fits using the molecular mass of I_2.

temperature dependence of the absorption area (f-factors) of the two subspectra is plotted in Fig. 2 together with fits of Debye temperatures. When taking into account the different f-factors of the two sites (see discussion below), the actual ratio of the two sites is close to unity (1 : 0.9(1)).

DISCUSSION OF THE MÖSSBAUER DATA

The present ^{129}I-Mössbauer data of the two subspectra in $C_{60}I_{3.64}$ can be interpreted in two ways as originating from (i) one (diatomic) molecule with two inequivalent sites or from (ii) two different (diatomic) molecules with equivalent sites (for a discussion, see Ref. 9). In both cases the different sites/molecules are modified by different local surroundings and interactions with neighbouring C_{60} or iodine molecules. From a Townes-Dailey plot of the observed isomer shift and quadrupole interactions [9], one derives for iodine on site 1 a deficit of 0.17 and for iodine on site 2 a surplus of 0.19 p-electrons with respect to iodine in molecular I_2 (see Tab. 1). This shows that the dominant effect of intercalation on the iodine species is a charge redistribution (polarization) between the two iodine sites and not a charge transfer from the C_{60} matrix.

The temperature dependence of the f-factors shown in Figure 2 gives additional information on possible locations of the two iodine sites in the lattice. Applying the Debye model of a (harmonic) solid and treating iodine as a (rigid) molecule with the mass $2 \cdot 129\ m_u$, we derive for site 1 a molecular Debye temperature of Θ_D = 72(3) K. Site 2 exhibits a lower molecular Debye temperature (Θ_D = 54(3) K), but the fit does not describe the data as well as in the case of site 1. There is strong evidence from the f-factor data of site 2 (and from the XRD data given below) that additional (librational) motions of the I_2 molecule, which are not included in the simple Debye model, contribute to the f-factor of site 2 in the low temperature range.

Additional information about the location of the iodine molecules is obtained from the Goldanskii-Karayagin effect (GKE) [12], observed in the quadrupole spectra of both sites and pointing to rather different vibrational anisotropies. For site 1 a polarization angle of 60(1)° is observed at 78 K (instead of 54.7° expected for a polycrystalline absorber). This points to an enhanced vibrational movement along the molecular axis, a behaviour also observed for halogen molecules in graphite intercalation compounds [10]. Site 2 exhibits a polarization angle of 40(2)° at 78 K, indicating a large vibrational anisotropy perpendicular to the molecular axis (see Tab. 1). When expressed by $R_{GKE} = \langle x^2\rangle/\langle z^2\rangle$, one derives R_{GKE} = 0.56 for site 1 and R_{GKE} = 2.5 for site 2. This is quite an unusual behaviour for a diatomic molecule, if we suggest that the one-molecule model is valid, and it must be connected with the location of this site in the C_{60} lattice. The structural model presented in the following can, however, convincingly explain all dynamic properties (f-factors and vibrational anisotropies) of both sites in the one-molecule model.

DISCUSSION OF THE XRD DATA

The results for the location and vibrational amplitudes of the iodine sites in the hexagonal lattice as obtained from a XRD structural refinement of a single-crystal of $C_{60}(I_2)_{\sim 2}$ [14] are shown in Fig. 3 and Fig. 4. One should mention in the beginning that the simple hexagonal arrangement of the C_{60} molecules leaves more space for interstitials in the *a-b* plane between the C_{60} layers than present at the octahedral and tetrahedral interstices in the *fcc* structure of pristine C_{60}. This property allows the insertion of molecules, like I_2, which are too large to fit into *fcc* C_{60}. The interstitial sites are located, as shown in Fig. 3, near the center (body-centered, *bc*) or near the faces (face-centered, *fc*) of a prisma formed by six C_{60} molecules. These sites are rather different in their dimensions. Using a simple hard-sphere model with 5 Å for the radius of the C_{60} molecules (r = 3.54 Å plus the van der Waals-radius of the C atoms), one finds a radius 2.64 Å for the (six-fold coordinated) *bc* site. For the (four-fold coordinated) *fc* site, which is actually the site with minimum distance to the 4 neighbouring C_{60} molecules, one derives a hard-sphere radius of 2.06 Å. Location of an iodine at a *fc* site would result in a minimum I-C distance of about 3.5 Å (depending, of course, on the relative orientation of the C_{60} molecule). This distance is slightly smaller than I-C distances of ~3.7 Å found in IBr- and ICl-graphites [11]. Since the location of iodine is actually displaced in the *a-b* direction from the unstable *fc* position, one ends up with I-C distances well comparable to those in ICl- and IBr-graphite. For a *central* location of iodine on the *bc* site, on the other hand, one derives I-C distances of ~4.1 Å, which are too large for a stable iodine position (that means that iodine would not contact any of the six surrounding C_{60} molecules). The actual position of iodine on the bc site is therefore displaced from the center in *a-b and* in *c*-directions with 6 possible locations. Because of these off-center positions, one expects very large and anisotropic vibrational amplitudes for the *bc* sites. This is actually observed in the XRD measurements and shown in Fig. 4. It is important to note that these displacements are more pronounced along the crystallographic *c*-axis and perpendicular to the molecular axis of the I_2 molecules (R_{XRD} = 2.6(3) at 300 K). The *fc* sites, according to the closer coordination with C_{60} molecules, exhibit smaller vibrational amplitudes with the largest component of the vibrational ellipsoid parallel to the *a-b* plane and along the molecular axis (R_{XRD} = 0.5(1) at 300 K).

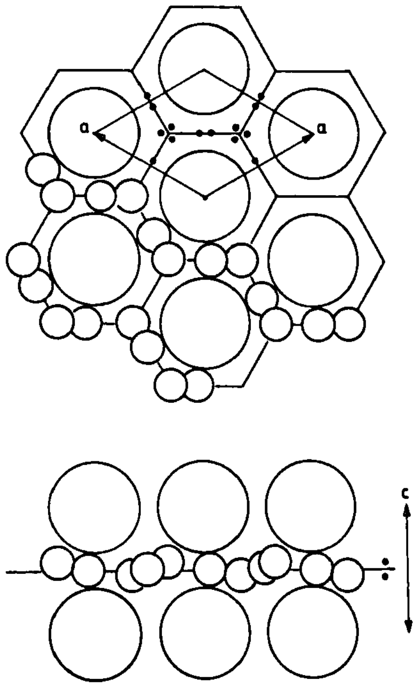

Fig. 3: Schematic crystal structure of $C_{60}(I_2)_{\sim 2}$ with respect to the iodine location from an XRD study of a single crystal at 300 K. (a) Projection of the iodine locations in the a-b plane seen along the c-axis and (b) in the a-b plane seen perpendicular to the c-axis (from [14]). The iodine atoms located on the corner of the hexagons (bc sites) correspond to site 2, the iodine atoms near to the middle of the hexagon sides (fc sites) correspond to site 1 of the Mössbauer spectra.

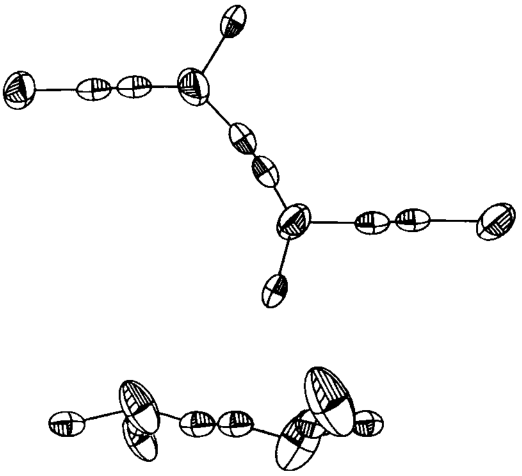

Fig. 4: Structural arrangement and vibrational amplitudes of the iodine sites in the hexagonal lattice of $C_{60}(I_2)_{\sim 2}$; same presentation as in Fig. 3 (from [14]).

COMPARISION OF MÖSSBAUER AND XRD DATA

Comparing the different vibrational behaviour for the two sites derived both from the Mössbauer and XRD data, one can immediately answer the questions about the iodine location and whether one or two molecular species are present [9]. All properties of the two sites observed in the Mössbauer spectra find their correspondence in the two locations (*fc* and *bc*) of iodine depicted in Figs. 3 and 4. Site 1 from the Mössbauer data is the *fc* site with an axially-symmetric quadrupole interaction, a relatively strong bonding due to the neighbouring C_{60} molecules and a larger vibrational amplitude along the molecular axis. Site 2 corresponds to the *bc* site and exhibits an asymmetric quadrupole interaction, since the neighbouring I_2 molecule is seen under an angle of 120°, a smaller bonding strength and large vibrational anisotropies perpendicular to the molecular axis. It is obvious from Fig. 3 that only one I_2 molecule is needed to account for the properties derived for both sites. By inserting I_2 molecules on possible sites, one derives some structural aspects of the intercalate arrangement: (i) The inserted I_2 molecules must form a chain structure (each iodine atom has one intramolecular and one intermolecular iodine neighbour). Chain structures are often found for halogen molecules in their solid or intercalated forms. (ii) Such a chain arrangement seems to be further stabilized by the dipole moments induced in the intercalated molecules (according to the Mössbauer results every I_2 molecule exhibits an intramolecular charge transfer of $\sim$0.18 electrons, see Tab. 1). (iii) The ideal stoichiometry of this structure is $C_{60}(I_2)_2$, resulting in a full occupation of the *bc* sites and a 2/3 occupation of the the *fc* sites. Any disorder in the chain arrangement leads to additional unoccupied interstices, which explains the observed iodine stoichiometries smaller 4.

Finally we want to mention that in undersaturated $C_{60}I_x$ systems one expects the appearance of isolated I_2 molecules. Preliminary Mössbauer results on a $C_{60}(I_2)_{1.22}$ sample gave evidence for an additional (isolated) I_2 site [15]. Further XRD studies will be performed at lower temperatures; we expect that order transitions may occur in the I_2 intercalate layers at lower temperatures.

In conclusion we derived for $C_{60}(I_2)_{\sim 2}$ from Mössbauer and XRD studies the location of iodine in the C_{60} lattice. The two iodine atoms of the I_2 molecules reside on two different lattice sites with different binding strength and vibrational dynamics. The iodine molecules form a chain structure in the C_{60} lattice. There is only a small charge transfer between C_{60} and iodine, but considerable charge redistribution within the intercalated I_2 molecule. These properties are typical for an inclusion compound of clathrate type.

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Table 1: Hyperfine parameters (at 4.2 K) and derived quantities for $C_{60}I_{3.64}$. S: isomer shift rel. to ZnTe; $\nu_Q = eQV_{zz}/h$: quadrupole coupling constant (converted to ^{127}I); η: asymmetry parameter, Θ_D: molecular Debye temperature; h_p : number of holes in the iodine 5p shell; $<z^2>$ and $<x^2>$: mean squared vibrational amplitudes parallel and perpendicular to the I_2 molecular axis at 78 K.

	$C_{60}I_{3.64}$		solid I_2
	Site 1	Site 2	
S (mm/s)	1.21(1)	0.68(1)	0.99(1)
ν_Q (MHz)	- 2607(10)	- 1845(10)	- 2195(10)
η	0.00(1)	0.305(5)	0.176(2)
h_p	1.17	0.81	1.02
Θ_D (K)	72(1)	54(2)	60 [Ref. 13]
$<x^2>$ (10^{-3} Å)	7(1)	20(2)	
$<z^2>$ (10^{-3} Å)	12(1)	8(1)	

References and Footnotes:

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