Tunneling States in Pt_2C_{60} Assigned by Magnetic Relaxation Measurements

M. H. Herbst[*], N. M. Pinhal, N. V. Vugman
Instituto de Física - UFRJ

C. Magon, A. J. C. Filho
Instituto de Física -USP- São Carlos

Abstract: *Electron spin-lattice relaxation times for Pt_2C_{60}, an amorphous solid showing paramagnetic centers distributed randomly over ca. 1% of fullerene molecules, were measured in the $7 - 100K$ temperature range. Attempts to fit the whole data to a Raman process were unsuccessful. We therefore invoke a more general frequency dependence in the form of a power law, where Raman rate varies with T as $1/T_{1Raman} \propto T^{n+\alpha}$. This affords $\alpha = 0.60$ for the low temperature data. Above 75K we found an exponential factor of 3.9 ± 0.5. From the experimental exponents it is clear that, for sufficiently low temperatures, $1/T_1 \propto T^{1+\alpha}$, which supports a model where an ensemble of two-level systems (TLS) with a continuous distribution of energy splittings and potential barriers between the two levels, is responsible for the spin-lattice relaxation. On the other hand, at temperatures above ~ 75K the experimental data show a curvature. The spin-lattice relaxation rate increases quite sharply, suggesting activation of new relaxation pathways. These new pathways can be assigned to a motion-induced contribution to the spin-lattice relaxation, probably due to temperature-dependent collective modes of the entire lattice or to temperature-induced conformational changes. This suggests that the structure of the title compound is mainly formed by chains with a distribution of conformational isomers.*

Amorphous solids have physical properties particularly different from those of crystalline matter at low temperatures, and it is now well established that amorphous solids present extra low energy excitations not present in crystalline media[1]. As a practical consequence, the temperature dependence of the spin-lattice relaxation rate is different in amorphous materials from that in single crystals, because the former show a distribution of the parameters characterizing the interactions among magnetic centers. In spin-lattice relaxation experiments, a *quasi*-linear temperature dependence of the $1/T_1$ relaxation rate is observed for amorphous solids. This data leads to the theoretical suggestion that they are mainly formed by tunneling systems (that is, two level systems, TLS) that interact with phonons. Notwithstanding, the general case of spin-lattice relaxation due to tunneling systems was derived by Murphy[2] in his classical paper. As an example, Balzer-Jöllenbeck *et al.*[3] have investigated by solid state NMR the temperature dependence of nuclear spin relaxation for different nuclear probes in a variety of inorganic glasses in the 1.5 to 300K temperature range. They found that below about 200 K the data can be interpreted consistently in the framework of thermally-activated excitations of disordered modes (TLS). Additionally, they suggested that in the glasses they analyzed a TLS is not formed by a single atom occupying two energetically slightly different positions, but arises from a rather large group of atoms possessing two conformations of nearly equal

[*] herbst@if.ufrj.br

energy. In an early paper concerning the study of fullerene anions in frozen solvent glasses, Schell-Sorokin et al.[4] studied by EPR methods, namely saturation recovery and ESE, calcium salts of C_{60}^-. It was observed a rather linear temperature dependence of $1/T_1$ at low temperatures. Nevertheless, they did not attempt to interpret the results in terms of tunneling systems, despite the fact that the fitting of the experimental recovery curve to a single exponential gave large standard deviations.

We report herein measurements of electron spin-lattice relaxation times in the 7 - 100K temperature range for Pt_2C_{60}, an amorphous solid showing paramagnetic centers distributed randomly over *ca.* 1% of the fullerene molecules. The synthesis and further characterization of the title compound are described elsewhere[5]. Electron spin-lattice relaxation measurements were performed in a

Bruker ELEXSYS E580 at the Laboratório de Biofísica - IFSC - USP.

Figure 1 is a log-log plot of the $1/T_1$ *versus* T data for Pt_2C_{60}, in which two distinct regions (7 - 75K and 75 - 100K) are clearly seen. Attempts to fit the whole data set to a two-phonon Raman process (T^9 dependence of the vibrational density of states) failed, so we invoke a more general frequency dependence of the vibrational density of states. In the low temperature region the Raman rate varies with T as

$$1/T_{1Raman} \propto T^{1+\alpha},$$

where the α coefficient can be obtained by the fit procedure, and usually is $0 < \alpha < 1$. The fitting of the relaxation data using non-linear least-squares to a $T^{1+\alpha}$ power law affords $\alpha = 0.60$ for the low temperature data. Above about 75K we found an exponential factor of 3.9 ± 0.5, the origin of which we discuss below.
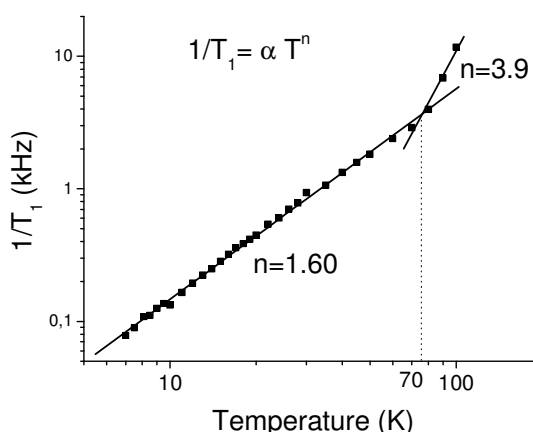

$$1/T_1 = \alpha T^n$$

n=3.9

n=1.60

Figure 1. Log-log plot of the $1/T_1$ *versus* T data for Pt_2C_{60}.

From the experimental exponents, it is clear that, for sufficiently low temperatures, $1/T_1 \propto T^{1+\alpha}$, supporting a model where an ensemble of two-level systems (TLS) with a continuous distribution of energy splittings and

potential barriers between the two levels, is responsible for the spin-lattice relaxation. However, at higher temperatures the experimental data shows a curvature; the spin-lattice relaxation rate increases quite sharply,

suggesting that above ~ 70K new relaxation pathways are activated. We speculate about this observation, and suggest that it can be assigned to a motion-induced contribution to the spin-lattice relaxation, probably due to temperature-dependent collective modes of the entire lattice or to temperature-induced conformational changes. The experimental data suggest that the structure of the title compound is mainly formed by chains with a distribution of conformational isomers and that the prevailing spin-lattice relaxation mechanism in Pt_2C_{60} is given by thermally activated excitations of TLS at low temperatures. The microscopic origin of these excitations and the exact process of relaxation of electronic spins are a matter of further investigations.

References

1. B. Golding, J. E. Graebner, in *Topics in Current Physics 24 – Amorphous Solids*, Phillips, W.A. Ed., Springer-Werlag, Berlin, 1981.
2. J. Murphy, *Phys. Rev.* **145** (1966) 241.
3. G. Balzer-Jöllenbeck, *Solid State Commun.* **65** (1988) 303.
4. A. J. Schell-Sorokin, *Chem. Phys. Lett.* **195** (1992) 225.
5. M. H. Herbst, *J. Non-Cryst. Solids* **272** (2000)127.