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# Low-temperature bistability in the magnetic properties of solvent-including lanthanide metallofullerene crystals

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Single crystals of the endohedral La@$C_{82}(CS_2)_{1.5}$ have been investigated by ESR, SQUID, and optical absorption measurements. We find that the crystal is a localized paramagnet at room temperature with evidence of strong antiferromagnetic interactions ($\theta \sim -130$ K). ESR spectroscopy reveals evidence of a phase transition at 150 K, that we assign to be an orientational ordering transition of the fullerene molecules. Furthermore, at low temperatures we find a magnetic bistability that can be controlled by the cooling rate. Investigations of Ce@$C_{82}(CS_2)_{1.5}$ reveal evidence of similar bistability and hence we postulate that it is a common phenomena in these endohedrals.

Metalloendohedral fullerenes represent an interesting and challenging variety of fullerene molecules. Fundamental interest in the solid state derives from the intrinsic charge transfer from the endohedral metal to the fullerene cage, which could lead to exciting electronic properties, as seen in fullerene metal intercalates;[1] from the exotic structural nature of the clathrated endohederal atoms; and from the existence of a molecular dipole moment.

The archetypal metallofullerenes Ln@$C_{82}$, Ln =lanthanide, have been studied to varying degrees in solution and solid states.[2–4] Electronically most are established to be $[\mathrm{Ln}]^{3+}[C_{82}]^{3-}$ ion pairs. As a result $[C_{82}]^{3-}$ has a singly occupied molecular orbital and is paramagnetic. A coherent picture of the solid state electronic properties of even these endohedral fullerenes has not been attained. This is due to difficulties in isolating sample quantities large enough for reliable bulk physical measurement. Further, possibilities of multiple phases and or solvent inclusion have lead to some conflicting property reports. Clarification of solvent inclusion and phase purity is particularly important as it is likely that the electronic ground state will be modified by the spacing and packing of the endohedrals.

The solvent including phase of metallofullerene La@$C_{82}(CS_2)_{1.5}$ has been reported to crystallize in a doubled body centered cubic lattice with space group $I\overline{4}3d$.[5] In the structure the fullerene molecules are disordered at room temperature. However, there are indications that the $C_{82}$ cage long axes align along the crystal diagonal (1,1,1) directions with the endohedral metal atoms also displaced along the diagonal towards the fullerene cage edge. This structure can be compared with the recently reported face centered cubic lattice structure of the pure La@$C_{82}$ phase, which apparently shows a similar cage disorder at room temperature.[6] Furthermore, these high symmetry disordered structures contrast with the toluene solvated structures of Ln@$C_{82}$(toluene), where a low $P2_1$ symmetry results in a rotationally restricted cage structure.[7]

The electron spin resonance technique (ESR) has proven to be an invaluable tool in unraveling the sometimes complicated electronic and magnetic properties of doped fullerenes, that are often masked in bulk measurements.[8,10,11] However, there are no reports of temperature dependent ESR studies of metallofullerenes crystals.

In this paper we report an investigation of the electronic and magnetic properties of the solvent including metal endohedral single crystals of type Ln@$C_{82}(CS_2)_{1.5}$ for Ln =La and Ce, focusing on the lanthanum compound, using ESR, SQUID, and optical measurements. We find that at room temperature the compounds are localized Curie-Weiss paramagnets with the $[\mathrm{Ln}]^{3+}[C_{82}]^{3-}$ electronic state and consequently a single spin localized on the $C_{82}$ cage. Temperature dependent ESR measurements on La@$C_{82}(CS_2)_{1.5}$ reveal a structural phase transition close to 150 K. We postulate that the transition is the well known orientational ordering transition of fullerene compounds. Furthermore, by paying close attention to the cooling rate through the transition, we find two distinct magnetic states can be stabilized at low temperature: in short bistability. A SQUID magnetometry study of Ce@$C_{82}(CS_2)_{1.5}$ reveals a similar magnetic bistability in the compound. Hence, we postulate that bistability is a common phenomena in endohedrals of this type.

Pure samples of Ln@$C_{82}$ were prepared and isolated by carbon arc and HPLC methods and were further characterized by mass spectrometry. Crystals of Ln@$C_{82}(CS_2)_{1.5}$ were grown by a slow evaporation method. Typically, 2–3 mg of pure Ln@$C_{82}$ was dissolved in 10–20 mg distilled $CS_2$ in an $N_2$ box and allowed to evaporate slowly over 2–3 weeks. The resulting crystals were examined under the microscope and found to be predominantly of two morphology types; a rhombohedral type and an obloid needle like type. X-ray diffraction measurements revealed that rhombohedral morphology crystals exhibited diffraction patterns that were fully indexed on $I\overline{4}3d$, yielding the refined lattice parameters: Ln=La, $a=25.625$ Å; Ln=Ce, $a=25.722$ Å. The needle-like crystals showed extra reflections that could not be indexed even with symmetry relaxation and were reasoned to be of a nonsingle type. Individual single crystals of La@$C_{82}(CS_2)_{1.5}$ were placed in ESR tubes and sealed under ~100 Torr helium gas. ESR measurement was performed on a JEOL RE3 *X*-band ESR spectrometer with 100 kHz modulation and a microwave power of 1 mW. Because of the

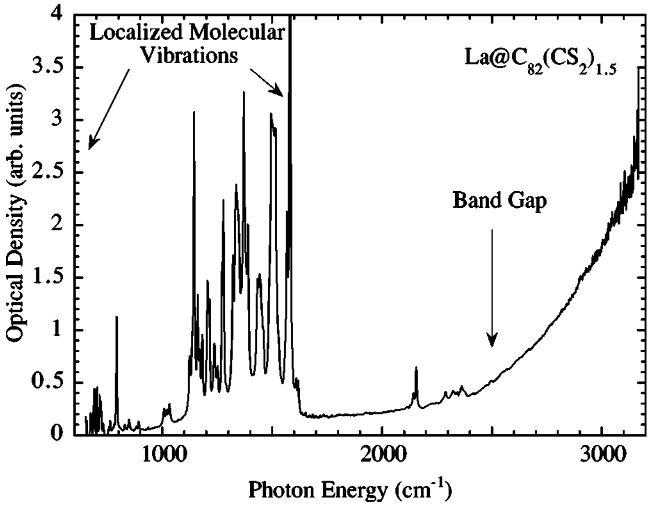

FIG. 1. Optical absorption spectrum of $La@C_{82}(CS_2)_{1.5}$ single crystals in the region 600–3200 $cm^1$.

roughly equivalent crystal dimensions and the cubic structure no attempt was made to control crystal alignment during experiments. SQUID measurements were performed on bulk ~1–2 mg selections of crystals.[9]

The optical absorption spectrum of single crystal $La@C_{82}(CS_2)_{1.5}$ is plotted in Fig. 1, recorded in the region 600–3200 $cm^{-1}$. Below 2200 $cm^{-1}$ the spectrum shows sharp absorption peaks indicative of localized molecular vibrations. There is no evidence of a Drude-like absorption behavior. Above 2500 $cm^{-1}$ the spectrum shows a broad onset of absorption indicative of bandlike electronic excitations. From the measurement we can infer a semiconducting state and the band gap to be around 2500 $cm^{-1}$.

The ESR signal of a typical $La@C_{82}(CS_2)_{1.5}$ crystal with rhombohederal morphology was recorded between 300 K and 4 K during a cooling cycle of around 8 to 12 h (slow cooling). The ESR signal was clearly a symmetric Lorenzian maintained throughout the temperature range and exhibited a pronounced narrowing towards lower temperatures. In a second experiment the crystal was rapidly cooled to 4 K via quenching into a precooled ESR cryostat, estimated maximum cooling time of around 10 minutes (fast cooling). The ESR signal was then recorded during slow warming to room temperature. In Fig. 2(a) the fitted Lorenzian half-widths for both experiments are plotted as a function of temperature. The measured signals at 4 K are compared in the inset. The $g$ factor was measured as 2.0012(2) at all temperatures in both experiments. The value is identical to that reported previously for $La@C_{82}$ ($g=2.001$) in solid and solution [2] and close to the free $\pi$-electron value. The $g$ factor and the symmetric Lorenzian line shape are consistent with a localized system with one unpaired electron on the $C_{82}$ cage. No systematic change in the $g$ factor with temperature could be determined within the resolution of the present data.

The slow cooling linewidth is approximately constant from room temperature until around 200 K where narrowing begins. A sharp drop-off in the linewidth with slow cooling can clearly be seen, narrowing rapidly below 160 K, becoming monotonic towards lower temperatures and finally remaining largely unchanged below 100 K. The behavior was found to be reversible upon warming the crystal. The low temperature line width after narrowing is around 25% of the high temperature value.

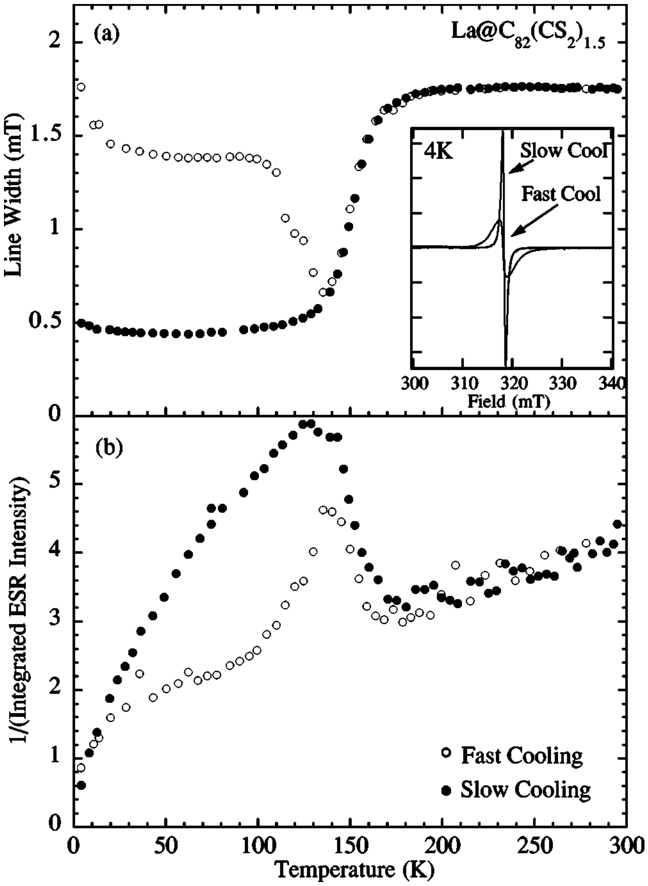

FIG. 2. (a) Temperature dependence of the fitted Lorenzian half-width of ESR spectra of $La@C_{82}(CS_2)_{1.5}$ crystals for fast and slow cooled experiments. The inset shows ESR spectra at 4 K. (b) Comparison of the temperature dependencies of the inverse integrated ESR susceptibilities.

The fast cooling line width closely follows the slow cooling behavior, with sharp narrowing down to 140 K. Below 140 K the widths diverge with the fast cooling width increasing sharply until around 100 K, where it has recovered near to 80% of its room temperature value. This is retained down to 30 K where it begins to increase again, with the second increase becoming rapid below 8 K. The two distinct temperature behaviors were observed reproducibly a number of times on the same crystal, and consistently for different crystals with the same rhombohedral morphology. The narrowing of the ESR line width (centered around 150 K) is evidence of a structural phase transition and will be discussed later.

The inverse integrated ESR spin susceptibility of single crystal is plotted as function of temperature in Fig. 2(b) for fast and slow cooling measurements. The slow cooled spin susceptibility is also plotted scaled to a slow cooled SQUID susceptibility measurement in Fig. 3. At high temperatures the susceptibilities follow the Curie-Weiss law. Fitting the SQUID or scaled ESR susceptibility between 200–300 K gives $C=0.46(0.1)$ $cm^3\,mol^{-1}\,K$ and $\theta=-130(20)$ K. The Curie moment is close to that calculated for a single localized paramagnetic electron (assuming $S=1/2$, $g=2.00232$; gives $C=0.385$ $cm^3\,mol^{-1}\,K$).

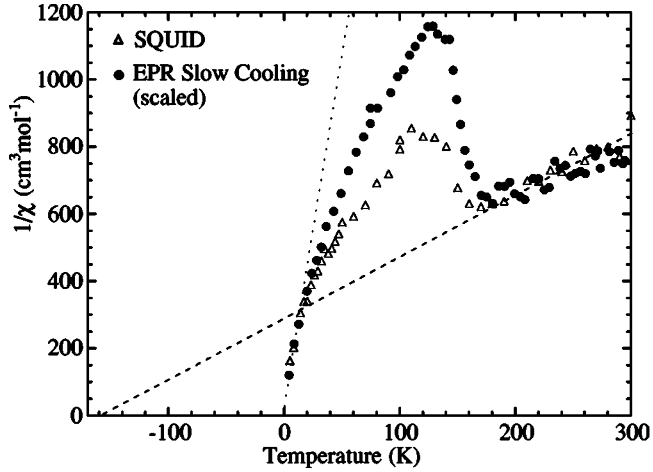

FIG. 3. Comparison of the inverses of SQUID and scaled integrated ESR susceptibilities of La@$C_{82}(CS_2)_{1.5}$ vs temperature after slow cooling.

The slow cooled susceptibility strongly deviates from the Curie-Weiss law below 180 K. The paramagnetic moment decreases sharply through the transition at 150 K, and begins to increase again only below 120 K. At low temperatures the measured paramagnetic spin can again be approximated as Curie-like. We estimate the Curie moment remaining as $C \sim 0.025\ \mathrm{cm^3\,mol^{-1}\,K}$ (fitting between 4–25 K), ~6% of the high temperature moment. The low-temperature susceptibility after fast cooling shows a similar large deviation from Curie-Weiss behavior below 180 K. However, below 100 K the high temperature Curie-Weiss behavior has returned. This is maintained down to 20 K where the Weiss moment is apparently lost and the susceptibility seems to follow the slow cooled behavior.

An unpaired electron on the fullerene cage makes ESR spectroscopy a valuable probe of the local dynamical and structural changes in La@$C_{82}(CS_2)_{1.5}$. The clear narrowing of the ESR linewidth (centered around 150 K) in La@$C_{82}(CS_2)_{1.5}$ is evidence of a structural phase transition that has significantly altered the average local environment of the fullerene molecules, on the ESR time scale, and hence changed the relaxation time. We propose that the transition is likely to be an orientational ordering of the $C_{82}$ fullerene molecules. This type of behavior has been observed before; for example, in $[\mathrm{TDAE}]^+[C_{60}]^-$[10] where an orientational ordering transition of $C_{60}$ molecules at around 150 K results in an anomalous narrowing of the ESR linewidth. In $[\mathrm{TDAE}]^+[C_{60}]^-$ single crystals[11] the form of the narrowing and the quantitative change, between 100–200 K, are similar to those we observe in La@$C_{82}(CS_2)_{1.5}$, indicating that the transitions are of a similar nature.

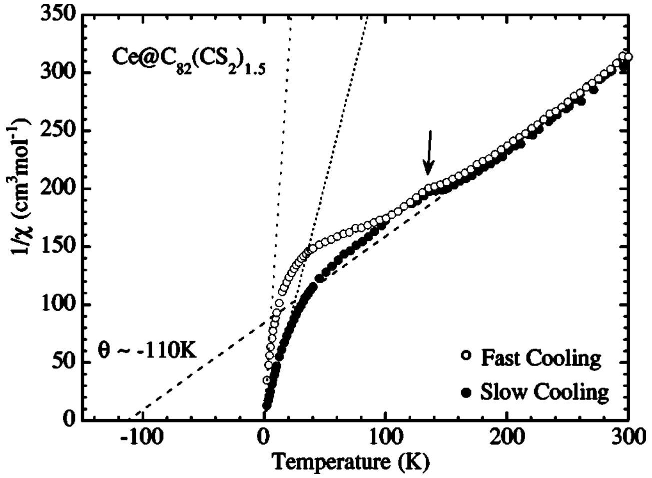

FIG. 4. Temperature dependence of the inverse SQUID susceptibilities of Ce@$C_{82}(CS_2)_{1.5}$ for fast and slow cooled experiments. The arrow indicates a small maximum at 130 K similar to that seen in La@$C_{82}(CS_2)_{1.5}$.

The recovery of linewidth after fast cooling to almost its high-temperature value is interesting: using the above reasoning we could say that the high-temperature rotational disorder of the molecules is retained down to the lowest temperatures as a result of fast cooling. This argument is based on there being insufficient alignment time, during fast cooling, for the molecules to align and hence the high-temperature dynamic disorder is replaced by frozen disorder below 100 K. However, this neglects that the linewidth, after fast cooling, first narrows with the slow cooling curve down to 140 K. In fact, it appears that rotational ordering is almost complete before it is destroyed. Hence, we argue that from a state of near full rotational order, fast cooling, results in a second transition (close to 140 K) to a state where almost complete rotational disorder is stabilized.

The large negative Curie-Weiss constant $\theta \sim -130$ K is evidence of strong antiferromagnetic interactions between spins on the fullerene molecules. Such strong interactions would be expected to give a bulk magnetic phase transition to antiferromagnetism. However, no clear evidence of a magnetic phase transition is observed, down to 2 K. In fact, after slow cooling the reduced Curie moment indicates quenching of the spin in the low-temperature phase. The small remaining moment is attributed to impurities and defects.

After fast cooling the Curie moment and the Weiss constant are retained in the low-temperature phase. This is consistent with the fullerene electron remaining localized on the cage. It is not unreasonable to argue that quenching of the fullerene unpaired electron moment requires an orientational order and hence when it is destroyed the localized moment is retained. However, a simple disorder of localized spins, can not explain the perceived absence of a magnetic transition at low temperatures. Indeed a persistent rotational disorder would be expected to produced a randomness in the interactions, possibly precipitating in a glassy magnetic order. It is possible that the increasing Lorentzian linewidth, below 30 K and the changing susceptibility behavior in this temperature region are related to a magnetic transition.

The study of La@$C_{82}(CS_2)_{1.5}$ crystals and the clear bistability enthused us to examine the structurally analogous crystals Ce@$C_{82}(CS_2)_{1.5}$ similar effects. Unfortunately crystals of Ce@$C_{82}(CS_2)_{1.5}$ were found to be ESR silent down to low temperatures. Alternatively, a bulk SQUID measurement was performed on a ~3 mg sample of microcrystalline Ce@$C_{82}(CS_2)_{1.5}$. In this case we measured the sample during warming, after slow cooling over 12 h from 300 to 2 K. We also performed a fast cooling experiment in the SQUID magnetometer by quenching the sample directly to 4 K, and then measuring during warming from 2 to 300 K. The inverse susceptibility behavior is plotted for Ce@$C_{82}(CS_2)_{1.5}$

in Fig. 4. The susceptibilities of the cerium endohedral follow the Curie-Weiss Law between 200 and 300 K.

The fitted Curie moment at these temperatures is 1.33(0.1) $\mathrm{cm^3\,mol^{-1}\,K}$. This value corresponds quite well with that expected for the sum of a single *f* electron remaining on the cerium $\mathrm{Ce}^{3+}$ ion and a single electron on the $C_{82}$ cage $(0.385+0.8034=1.19\ \mathrm{cm^3\ mol^{-1}\ K})$. The apparent Weiss constant in this region is again large and negative, $\theta=-110(20)$ K. The fitted Curie moment and the analogous structure to $\mathrm{La@C_{82}(CS_2)_{1.5}}$ implies a similar localized electronic state for $\mathrm{Ce@C_{82}(CS_2)_{1.5}}$, as $[\mathrm{Ce}]^{3+}[\mathrm{C_{82}}]^{3-}$, at room temperature. The intimate nature of cerium and fullerene spins may be the cause of the ESR silence. Below 170 K, the susceptibility behaviors deviate from the Curie law, with a similar but less dramatic change than in $\mathrm{La@C_{82}(CS_2)_{1.5}}$, reaching a maximum at 130 K (see Fig. 4).

At low temperatures, using the Curie approximation, we estimate that the remaining moment (see Fig. 4) as C $\sim 0.057\ \mathrm{cm^3\,mol^{-1}\,K}$ after fast cooling and C $\sim 0.25\ \mathrm{cm^3\,mol^{-1}\,K}$ after slow cooling. Hence, in the case of $\mathrm{Ce@C_{82}(CS_2)_{1.5}}$ we see that low temperature behavior is similar to that of $\mathrm{La@C_{82}(CS_2)_{1.5}}$ with a bistability of the remaining paramagnetic moment. However, conversely the situation is reversed with a paramagnetic moment remaining after slow cooling and an almost complete quenching after fast cooling. Finally, we note that the qualitatively similar forms of the susceptibility curves in $\mathrm{Ln@C_{82}(CS_2)_{1.5}}$ (Ln $=$La, Ce) indicate that analogous transitions occur and are most likely the origin of the bistability.

The correlation between molecular orientation and electronic properties is one of the most intriguing and unique features that have emerged from the study of fullerene materials.[10] The present results, whilst leaving many open questions; for example, the exact nature of the structural phase transitions and the need for confirmation of a bulk magnetic transition at low temperatures, provide strong evidence that bistability effects are wide spread in metalloendohedral fullerenes and are related to orientation effects. For example, in a recent report of the magnetic properties of $\mathrm{Ho@C_{82}}$ and $\mathrm{Gd@C_{82}}$ (Ref. 12) attention to phase effects and cooling procedures may reveal further interesting properties.

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