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Christopher John Nuttall [a], Yasuhira Inada [a], Kiyoe Nagai [a], Youichiro Hayashi [a], Takahiro Kitani [a] & Yoshihiro Iwasa [a]

[a] Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa, 923-1292, Japan

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Magnetic Properties of Metal Endohedral Fullerene Crystals La@C_{82}·$(Cs_2)_{1.5}$

CHRISTOPHER JOHN NUTTALL, YASUHIRA INADA, KIYOE NAGAI, YOUICHIRO HAYASHI, TAKAHIRO KITANI and YOSHIHIRO IWASA

Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa 923–1292, Japan

We report a magnetic investigation of the endohedral metallofullerene La@C_{82}·$(CS_2)_{1.5}$. Firstly, pure La@C_{82} was prepared and isolated, then single crystals were grown by a slow evaporation method. The crystals were screened by x-ray diffraction measurements and the structure was confirmed to be a body centered cubic lattice $a = 25.62$Å with space group I-43*d*. Optical absorption measurement revealed the compound to be a localised insulating or semi-conducting with a band gap around 2500cm^{-1}. Temperature dependent EPR and SQUID measurements indicate that the high temperature magnetic behavior is that of a Curie-Weiss paramagnet, C = 0.4(+/-0.1)cm^{3}mol^{-1}K, which corresponds to a single spin localised on the C_{82} cage. Furthermore, a large negative Weiss constant, $\theta = -150$(+/-20)K, indicates the presence of strong antiferromagnetic interactions. EPR measurements show a sharp decrease in the line width occuring below around 160K, indicating a phase transition. The Curie moment appears to be lost at temperatures below 80K.

Keywords: endohedral metallofullerene; La@C_{82}; magnetism; phase-transition

INTRODUCTION

Endohedral metallofullerenes provide a new and interesting branch to fullerene chemistry having unique structural properties. The electronically reduced state of the endohederal fullerene molecule is reminiscent of fullerene intercalation compounds for which a huge variety of electronic ground states in the solid state have been discovered. Since the discovery and isolation[1] of the first endohederal fullerenes of type M@C_{82} {M = Y, Sc, La and Ce} a great deal of work

has been directed to improving the carbon arc synthesis processes, and HPLC isolation methods in order to improve their low yields. The low yield has severely restricted the number of reports on the physical properties of the materials.

FIGURE 1 The endohedral molecular structure of $La@C_{82}$.

In $La@C_{82}$ (see figure 1) the molecular electronic state is described formally as $[La]^{3+}[C_{82}]^{3-}$, with three electrons transferred to the C_{82} cage. The $La@C_{82}$ molecule has a singlely occupied molecular orbital, which is strongly localised on C_{82}. In the solid state X-ray diffraction investigations of $M@C_{82}$ endohedrals have been carried out on a number of examples, with or without co-crystallising solvent molecules.[2] In all the published studies the endohedral atom is displaced away from the centre of the fullerene cage close to the cage edge. Disorder of the fullerene cage is observed at room temperature for high symmetry structures, whilst for low symmetry structures e.g. $Y@C_{82}$.(toluene) the fullerene cage is ordered.[2b]

At this early stage of investigations the physical behaviour of the endohedrals in the solid state is still not clear. In this study we have synthesised and purified bulk quantities of $La@C_{82}$ endohedrals and grown solvent including single crystals of $La@C_{82}\cdot(CS_2)_{1.5}$. The structure of $La@C_{82}\cdot(CS_2)_{1.5}$ has been reported to be a doubled body centred cubic structure (I-43*d*, a = 25.727Å), with a large amount of disorder at room temperature.[2a] We have investigated $La@C_{82}\cdot(CS_2)_{1.5}$ single crystals with optical and magnetic measurements, in order to clarify the physical behavior.

EXPERIMENTAL

Samples of $La@C_{82}$ containing soot were obtained *via* the DC arc discharge of La_2O_3 loaded carbon composite rods under a partial helium

atmosphere of 200 torr. The $La@C_{82}$ containing soot was then extracted by refluxing in ortho-dichlorobenzene and then pyridine solvents. $La@C_{82}$ was then isolated by HPLC and characterised using TOF-mass and infrared spectrometry. Crystals of solvated $La@C_{82}$ were prepared by slow evaporation from saturated CS_2 solutions, under anerobic conditions. Typically 1-2 mg of pure $La@C_{82}$ was dissolved in distilled CS_2 (~10 cm^3) and the solution was decanted from any non-dissolving material. The evaporation was controlled to last 2-3 weeks and the precipitated products were examined under the microscope. Crystals with a simple single crystal morphology were removed. A few crystals were mounted on capillaries and examined by X-ray diffraction. The single crystal nature of the crystals was confirmed by the sharp brilliance of the reflections and that full indexation of the reflections was possible on the reported cubic I-43*d* structure, with refined lattice parameter $a = 25.616$Å.

EPR measurements were performed using a JEOL RE3 X-band ESR spectrometer with a 100kHz modulation and a microwave power of 1mW. Individual single crystal samples were sealed in EPR tubes under 100 torr of helium gas.

Room temperature infrared absorbtion spectra have been measured using a commercial FTIR spectrometer.

RESULTS AND DISCUSSION

The infrared absorbtion spectrum for $La@C_{82}·(CS_2)_{1.5}$ was recorded at room temperature between 500-3200cm^{-1}. Below 2200cm^{-1} the spectrum showed only sharp absortion peaks indicative of localised molecular vibrations. Above 2500cm^{-1} the spectrum showed a broad onset of absorbtion, indicative of band-like electronic excitations. From the measurement we can estimate the band gap in $La@C_{82}·(CS_2)_{1.5}$ to be around 2500cm^{-1}.

Figure 2 shows the temperature evolution of EPR spectra of $La@C_{82}·(CS_2)_{1.5}$ crystals. The spectra are symmetric and give a good fit to the Lorentzian function throughout the temperature range. The line width is essentially constant above 200K and begins to decrease towards lower temperatures, decreasing rapidly below 160K. Finally, the line width decreases monotonically to 100K, below which it becomes constant. This type of narrowing of the EPR line width is seen in

$[TDAE]^{+}[C_{60}]^{-}$ at 170K[3] and has been attributed to the commonly observed orientational ordering transition of fullerene molecules.

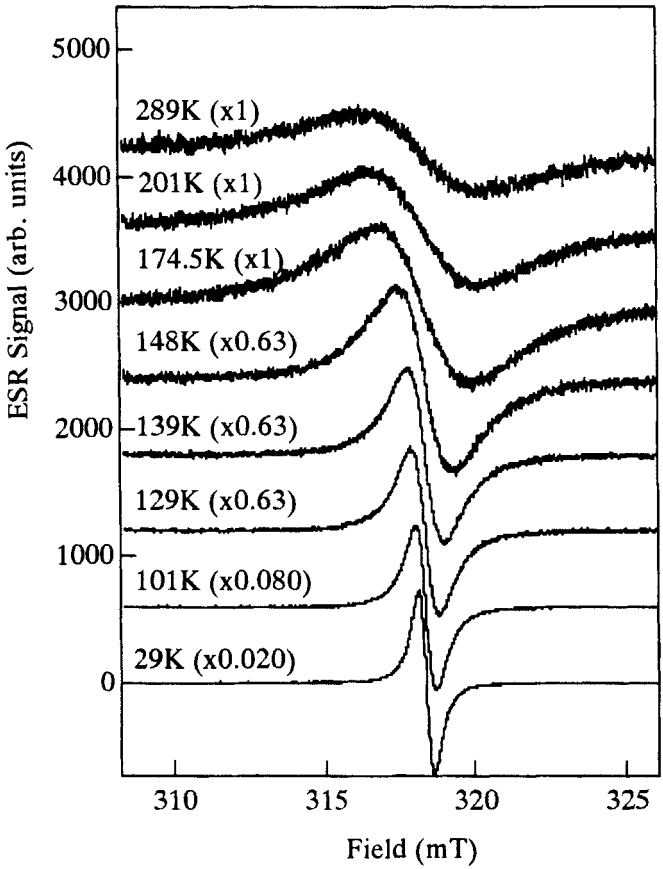

FIGURE 2 The temperature dependence of the ESR spectrum of $La@C_{82}\cdot(CS_2)_{1.5}$

The temperature dependence of the integrated spin susceptibility from the EPR data is plotted in Figure 3, scaled to the high temperature SQUID magnetisation. The susceptibilities from EPR and SQUID were

essentially identical at all temperatures. The high temperature susceptibility closely follows the Curie-Weiss law between 200-300K.

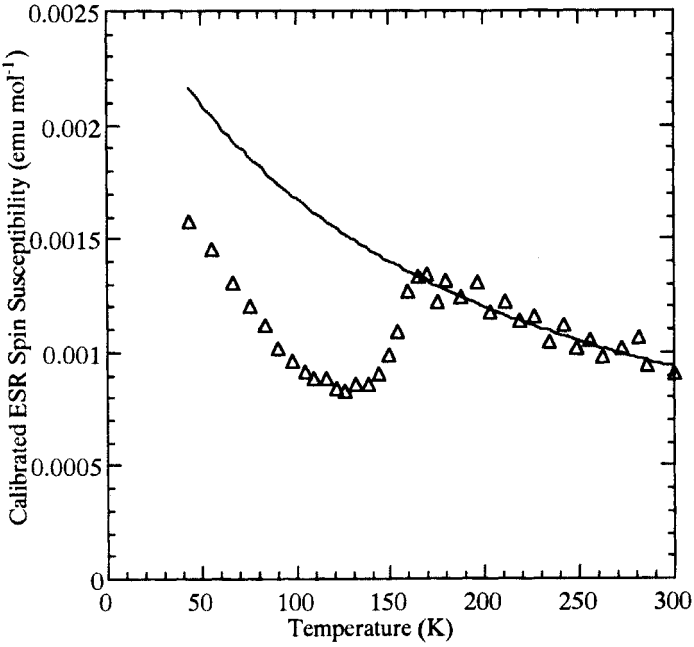

FIGURE 3 Calibrated EPR spin susceptibilities of $La@C_{82}\cdot(CS_2)_{1.5}$, fitted to Curie-Weiss law (200-300K).

Figure 3 shows the EPR spin susceptibility fitted to Curie-Weiss law between 200-300K, which yields the fitted parameters: C = 0.4(+/-0.1)$cm^3mol^{-1}K$ and θ = -150(+/-20)K. The Curie constant compares favourably to that expected for a single paramagnetic electron (s = 1/2, g = 2, gives C = 0.385$cm^3mol^{-1}K$). The large negative Weiss constant is indicative of strong antiferromagnetic interactions in the compound. The high temperature parmagnetic moment and the optically observed band gap (~2500cm^{-1}) provide supportive evidence that in $La@C_{82}\cdot(CS_2)_{1.5}$ the localised electronic state $[La]^{3+}[C_{82}]^{3-}$ of the molecules is maintained in the solid state with one unpaired electron strongly localised on the C_{82}

cage. This should be compared with the non-solvent including $Ce@C_{82}$ and $La@C_{82}$ compounds where the cage spin is delocalised at room temperature. Below 160K the paramagneic moment decreases sharply, coincidental with the observed narrowing of the EPR line width. At temperatures below 80K the moment again appears to be Curie-like. From the present data, we were able to estimate the low temperature Curie moment to be approximately 1/3 of its high temperature value and we also noted that the Weiss constant was completely lost.

In conclusion we have confirmed that the magnetic behaviour of room temperature $La@C_{82}\cdot(CS_2)_{1.5}$ is that of a localised s=1/2 paramagnet. A large negative Curie-Weiss constant (~-150K) indicates the presence of strong antiferromagnetic interactions between moments. Apon cooling there is a phase transition, seen by the narrowing of the EPR line width, which most likely corresponds to the orientational ordering of endohedral molecules. At temperatures below 80K the Curie moment appears to be quenched. The origin of the moment quenching and the phase transtion are being further investigated.

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