Spin frustration and magnetic ordering in the *S*=1/2 molecular antiferromagnet fcc-Cs_3C_{60}

Y. Kasahara[1*], Y. Takeuchi[1], T. Itou[1], R. H. Zadik[2], Y. Takabayashi[2], A. Y. Ganin[3,4], D. Arcon[5,6], M. J. Rosseinsky[3], K. Prassides[2,7], and Y. Iwasa[1,8†]

[1]*Quantum-Phase Electronics Center (QPEC) and Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan*

[2]*Department of Chemistry, Durham University, Durham DH1 3LE, UK*

[3]*Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK*

[4]*School of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK*

[5]*Jozef Stefan Institute, Jamova c. 39, 1000 Ljubljana, Slovenia*

[6]*Faculty of Mathematics and Physics, University of Ljubljana, Jadranska c. 19, 1000 Ljubljana, Slovenia*

[7] *WPI - Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

[8] *RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan*

We have investigated the low-temperature magnetic state of face-centered-cubic (fcc-) Cs_3C_{60}, a Mott insulator and the first molecular analog of a geometrically frustrated Heisenberg fcc antiferromagnet with S = 1/2 spins. Specific heat studies reveal the presence of both the long-range antiferromagnetic ordering and magnetically disordered state below T_N = 2.2 K, which is in agreement with local probe experiments. These results together with the strongly suppressed T_N are unexpected for conventional atom-based fcc antiferromagnets, thus implying that the fulleride molecular degrees of freedom give rise to the unique magnetic ground state.

PACS numbers:

75.30.-m	Intrinsic properties of magnetically ordered materials
75.40.-s	Critical-point effects, specific heats, short-range order
74.70.Wz	Carbon-based superconductors
76.60.-k	NMR and relaxation

Cubic alkali fullerides are a unique playground among organic materials since the energy scales of the band width (W), vibrational frequencies (ω_{ph}), and on-site Coulomb repulsion (U) are all comparable, thus determining the intriguing electronic states of degenerate t_{1u} frontier molecular orbitals [1,2]. For the recently discovered most expanded Cs_3C_{60}, the superconductivity with transition temperature T_c as high as 38 K [3] evolves directly from the ambient-pressure Mott-insulating state with applied pressure [3-8].

Antiferromagnetic (AFM) ordering of S = 1/2 spins localized on C_{60}^{3-} anions has been reported in nearly all expanded A_3C_{60} (A = alkali metal) compounds, including face-centered-cubic (fcc) and body-centered-cubic (bcc)-type A15-Cs_3C_{60} (with Neel temperatures T_N = 2.2 K and 46 K, respectively) [5,6,9], and face-centered-orthorhombic (fco-) $(NH_3)A_3C_{60}$ (T_N = 40-76 K) [2,10] or $(CH_3NH_2)K_3C_{60}$ (T_N = 11 K) [11-13]. In the case of fco structures, the lowering of crystal symmetry removes the t_{1u} molecular orbital degeneracy and C_{60} molecules are orientationally ordered, triggering AFM ordering of the orbitally ordered state. In view of the strongly suppressed T_N in the fcc-Cs_3C_{60} when compared to the A15 and fco structures, the importance of the geometrical spin frustration inherent to the fcc lattice has been suggested [6].

The fcc lattice with nearest neighbor (NN) Heisenberg antiferromagnetic exchange interactions is a textbook geometrically frustrated spin system with an infinite degeneracy of the ground state [14,15], but is known that AFM ordering usually occurs at relatively high T_N that is comparable to the NN exchange interactions [16-19]. On the other hand, suppression of AFM ordering is uncommon, and spin glasses and nonmagnetic ground states such as valence-bond glasses have been reported, e.g. in double perovskites where atomic orbital degeneracy and strong spin-orbit coupling play key roles [20]. In conventional systems, the constituent units of the fcc lattice are exclusively atomic basis, whereas those become the molecular C_{60}^{3-} anions with weak spin-orbit coupling in fcc-Cs_3C_{60}. Electron correlation localizes the electronic spins with S = 1/2 on C_{60}^{3-} anions due to the intramolecular

Jahn-Teller effect [21]. Moreover, C_{60}^{3-} anions adopt one of two orientations in a random way (merohedral orientational disorder) [22] in fcc-Cs_3C_{60} unlike in the orientationally ordered and non-frustrated A15 polymorph. Therefore, fcc-Cs_3C_{60} provides a new perspective on the frustrated fcc antiferromagnet with molecular (rather than atomic) internal degrees of freedom.

The AFM ordering in fcc-Cs_3C_{60} has been derived from the results of muon spin relaxation (μSR) experiments, which revealed coherent ordering of the C_{60}^{3-} spins on the length scale probed by the muons below 2.2 K together with severe spatial disorder and magnetic inhomogeneities accompanying spin freezing [6]. On the other hand, thermodynamic measurements have been missing though they are essentially required to provide compelling evidence for the ground state in this novel magnetic material. Especially, the specific heat measurements are critically important and would provide definitive information about the magnetic transition. It should be emphasized that the specific heat in A_3C_{60} has been reported only for K_3C_{60} in the last 20 years [23,24], as the extreme air-sensitivity of these compounds makes measurements exceptionally challenging.

In this Letter, we report a comprehensive macroscopic and microscopic study of the magnetic ground state in the frustrated fcc antiferromagnet Cs_3C_{60} by means of specific heat and nuclear magnetic resonance (NMR) measurements. The long-range AFM order below T_N, which is accompanied by the magnetically disordered state, was proved by the thermodynamic probe. The AFM transition is reminiscent of neither the simple classical nor the quantum fcc AFM ordering and it arises from the characteristic structural, molecular, and electronic properties of fcc-Cs_3C_{60}.

We first turn to the specific heat on Cs_3C_{60} samples. Details of synthesis and measurement procedures are given in Ref. [25]. The temperature dependences of the specific heat (C) for the fcc- and A15-Cs_3C_{60} polymorphs are compared in Fig. 1(a). Below 100 K, phonon contributions significantly

dominate C due to the molecular nature of the solids. In the disorder-free A15-Cs_3C_{60}, a shoulder-like anomaly is clearly discernible, which is consistent with the AFM transition at T_N = 46 K [5,8,9]. For A15-Cs_3C_{60}, there is no non-magnetic analog with identical crystal symmetry, which is required to subtract the phonon contribution and to extract the magnetic one. However, in C_{60} solids, the low temperature phonon contribution can be described by the combination of the Debye and Einstein expressions due to the librational, intermolecular, and intramolecular vibrations [23,26]. Therefore, the lattice contribution to C was estimated from a fit to such contributions at high temperatures well above T_N [25]. After its subtraction, we derived the magnetic specific heat C_m for A15-Cs_3C_{60} [inset of Fig. 1(a)]. C_m reveals a distinct peak at T_N in spite of the powder nature of the specimen, providing strong evidence for the long-range AFM ordering in the A15 polymorph. The magnetic entropy S_m was estimated by the relationship $S_m = \int_0^T (C_m/T)dT$. S_m reaches 1.8 J/Kmol at 60 K, which is about 30 % of the expected value of $R\ln(2S+1)$ with S = 1/2. Taking into account the A15 phase fraction in the present sample, ~57 %, most of the magnetic entropy is indeed released at the transition. These results support Jahn-Teller distortion of C_{60}^{3-} anions [21], which is required for the low-spin S = 1/2 state of C_{60}^{3-} anions. On the other hand, in contrast to the A15 polymorph, C/T monotonically decreases with decreasing T in the fcc polymorph, and there is no distinct anomaly at the reported T_N ~ 2.2 K even if C/T is plotted as a function of T^2 [Fig. 1(b)].

In an effort to extract the magnetic specific heat, an isosymmetric superconducting sample with composition, $Rb_{0.35}Cs_{2.65}C_{60}$ (T_c = 27 K) [27], where both electrons and phonons contribute to C, was measured. As shown in Fig. 2(a), $C/T(T)$ for the magnetic and SC compounds coincide with each other except for around T_c, implying that the phonon contributions are nearly identical in both compounds. Careful comparison of the specific heat at low temperatures [Fig. 2(b)] reveals a difference between C for the magnetic insulator and that for the superconductor, most likely originating from a reduction of the electronic contributions in the SC state. In the BCS

SC state, it has been shown that the electronic specific heat almost vanishes at low temperatures below $T/T_c \sim 1/7$ (~ 4 K for $Rb_{0.35}Cs_{2.65}C_{60}$) due to the condensation of electron pairs [25,28], and thus, only the phonons contribute to the specific heat in the superconductor at low temperatures. Therefore, we estimated C_m by subtracting the total C for the superconductor from that for fcc-Cs_3C_{60}.

The temperature dependence of C_m/T is shown in Fig. 3(a). C_m/T exhibits a broad anomaly with a maximum close to T_N, which is in marked contrast with a simple AFM ordering where a λ-like anomaly would be observed at T_N. The broad feature is typical of spin freezing in a random configuration with short-range spin correlations. The $C_m(T)$ data in Fig. 3(b) are also markedly reminiscent of those in spin-glass compounds such as the geometrically frustrated pyrochlore $Y_2Mo_2O_7$ [29]. However, $C_m(T)/T$ well below T_N shows T^2-dependence in addition to a residual linear term that is expected for spin glasses [Fig. 3(c)] [29], indicating that the ground state is not a canonical spin glass. The T^3-dependence of $C_m(T)$ is ascribed to magnon excitations for a long-range AFM ordering in three dimensions [30]. Therefore, specific heat provides thermodynamic evidence for the long-range AFM ordering below T_N, and reveals the presence of both the AFM ordering and a glass-like magnetically disordered state in the ground state.

To elucidate the magnetic ground state microscopically, we additionally performed NMR measurements down to 1.5 K [25]. Figure 4(a) shows the ^{133}Cs NMR spectra at 196 K and below 5 K. The spectrum at 196 K is composed of four distinct peaks attributed to octahedral and tetrahedral peaks [6,8,31]. With decreasing temperature, the ^{133}Cs NMR peaks exhibit significant broadening [6,8,25,31] to nearly 5000 ppm at 1.5 K in both positive and negative frequencies. This reflects the development of large static local magnetic fields at the ^{133}Cs sites originating from the closest C_{60}^{3-} electronic moments with antiferromagnetic correlations between the NN C_{60}^{3-} sites.

Figure 4(b) displays the nuclear spin-lattice relaxation curves, measured at the peak position of the main broad NMR spectra. The relaxation curves show non-linear behavior in the semi-log plot, indicating the presence of magnetic inhomogeneities. We employed two methods for estimating T_1: (i) a stretched exponential model in order to account for the T_1 distribution [solid lines in Fig. 4(b)], and (ii) a simple exponential model using only the initial decay slopes of the relaxation curves. Figure 4(c) shows the temperature dependence of $1/T_1$ as derived from both methods, showing qualitatively the same temperature dependence. $1/T_1$ shows a broad maximum at around 2.5 K, which is in sharp contrast to conventional AFM order [5,31], where $1/T_1$ usually exhibits a divergent behavior at T_N. The decrease in $1/T_1$ with keeping the stretch exponent α unchanged below T_N provides another hallmark of the AFM order with persistent magnetic inhomogeneities down to low temperatures.

Although the present specific heat and NMR experiments show there are no sharp anomalies in fcc-Cs_3C_{60}, the long range AFM ground state is proved by the T^3-term in C_m. The frozen fraction estimated from S_m below 2.5 K is below 5 %, resulting in the absence of clear signature of long-range order in both the specific heat and NMR relaxation rate. Importantly, the specific heat confirms the bulk static magnetic ground state in fcc-Cs_3C_{60} unlike NMR and μSR experiments with faster time windows of the probes. It should be noted that the previous μSR [6] and present NMR experiments show no signature of macroscopic phase separation. Therefore, thermodynamic and local probes provide compelling evidence for microscopic coexistence of AFM ordering and disordered spin state below T_N in fcc-Cs_3C_{60}.

In frustrated fcc Heisenberg antiferromagnets with weak spin-orbit coupling, a general consensus is that thermal or quantum fluctuations and quenched disorder can stabilize long-range AFM order at ~ $0.4J/k_B$ (J is the NN exchange interaction) [16-18,32,33], in contrast with the observed T_N that is one order smaller than J/k_B ~ 30 K [6]. For quantum spin systems, spin liquid and valence-bond glass states have also been suggested [34,35].

However, these can be ruled out due to the presence of a static internal magnetic field at low temperatures. Therefore, the AFM order with suppressed T_N as well as inhomogeneous magnetic ground state is not comparable to conventional theories, making the present system a unique example among the frustrated fcc antiferromagnets.

To understand the nature of the magnetic transition in fcc-Cs_3C_{60}, we should take into account the fulleride molecular degrees of freedom, which have never been considered in conventional model systems based on atoms, i.e. Jahn-Teller coupling in C_{60}^{3-} anions and the orientational disorder. In the pyrochlore lattice, it has been proposed that strong exchange (or bond) randomness suppresses the long-range AFM ordering and induces a spin-glass phase [36]. Such randomness is relevant here with respect to the orientational disorder of C_{60}^{3-} anions, which changes C_{60}-C_{60} NN contacts and introduces random distribution in the NN exchange [37]. Another possible factor is the effect of electron correlations. This reminds us of $S = 1/2$ triangular antiferromagnets, where the NN Heisenberg model has found long-range ordering [38], but the quantum spin liquid state is indeed realized in organic charge-transfer salts [39]. It is believed that key properties to suppressing long-range order and realizing the quantum spin liquid are the spin frustration and the proximity to the Mott transition boundary [39]. In this context, it is reasonable to assume that the same factors contribute to the reduced T_N because fcc-Cs_3C_{60} shows a transition from the Mott insulator to metal at low pressure similarly to the charge-transfer salts. Although supporting theories for the present scenario do not exist, we suggest the frustrated fcc lattice and internal molecular degrees of freedom give rise to a unique magnetic ground state among fcc antiferromagnets.

In conclusion, the fcc-Cs_3C_{60} is a Mott-Jahn-Teller insulator with $S = 1/2$ spins located on orientationally disordered C_{60}^{3-} anions and the first example of a frustrated fcc Heisenberg molecular antiferromagnet. Specific heat provides thermodynamic evidence that a tiny portion of electronic magnetic

moments undergo the long-range AFM ordering, which is accompanied by randomly disordered magnetic states. The unique magnetic ground state is not comparable to that predicted by simple classical or quantum theories for the conventional systems based on atoms, and the effects of characteristic structural, molecular, and electronic properties of fcc-Cs_3C_{60} have been discussed.

We would like to thank Y. Motome for fruitful discussions. This work was supported in part by Grants-in-Aid for Specially Promoted Research (No.25000003) and for Young Scientists (B) (No.2474022), the "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)" from JSPS, Japan, and SICORP-LEMSUPER FP7-NMP-2011-EU-Japan project (No.283214). K. P. and M. J. R. thank EPSRC for support (EP/K027255 and EP/K027212). D. A. also acknowledges the support of the Institute of Advanced Study and Chemistry Department, Durham University through the award of a Durham International Senior Research Fellowship. K. P. thanks the Royal Society for a Wolfson Research Merit Award. MJR is a Royal Society Research Professor.

*kasahara@ap.t.u-tokyo.ac.jp
† iwasa@ap.t.u-tokyo.ac.jp

[1] O. Gunnarsson, Rev. Mod. Phys. **69**, 575 (1997).
[2] Y. Iwasa and T. Takenobu, J. Phys.: Condens. Matter **15**, R495 (2003).
[3] A. Y. Ganin *et al.*, Nature Mater. **7**, 367 (2008).
[4] G. R. Darling, A. Y. Ganin, M. J. Rosseinsky, Y. Takabayashi, and K. Prassides, Phys. Rev. Lett. **101**, 136404 (2008).
[5] Y. Takabayashi *et al.*, Science **323**, 1585 (2009).
[6] A. Y. Ganin *et al.*, Nature **466**, 221 (2010).
[7] Y. Ihara *et al.*, Phys. Rev. Lett. **104**, 256402 (2010).
[8] Y. Ihara *et al.*, Europhys. Lett. **94**, 37007 (2011).
[9] P. Jeglic *et al.*, Phys. Rev. B **80**, 195424 (2009).
[10] K. Prassides *et al.*, J. Am. Chem. Soc. **121**, 11227 (1999).
[11] Y. Takabayashi, A. Y. Ganin, M. J. Rosseinsky, and K. Prassides, Chem. Commun., 870 (2006).
[12] A. Y. Ganin *et al.*, J. Am. Chem. Soc. **128**, 14784 (2006).
[13] D. Arcon, A. Y. Ganin, Y. Takabayashi, M. J. Rosseinsky, and K. Prassides, Chem. Mater. **20**, 4391 (2008).
[14] P. W. Anderson, Phys. Rev. **79**, 705 (1950).
[15] T. Oguchi, H. Nishimori, and Y. Taguchi, J. Phys. Soc. Jpn. **54**, 4494 (1985).
[16] C. L. Henley, J. Appl. Phys. **61**, 3962 (1987).
[17] H. T. Diep and H. Kawamura, Phys. Rev. B **40**, 7019 (1989).
[18] M. V. Gvozdikova and M. E. Zhitomirsky, JETP Lett. **81**, 236 (2005).
[19] M. S. Seehra and T. M. Giebultowicz, Phys. Rev. B 38, 11898 (1988).
[20] G. Chen, R. Pereira, L. Balents, Phys. Rev. B 82, 174440 (2010).
[21] G. Klupp *et al.*, Nature Comm. **3**, 912 (2012).
[22] A. P. Ramirez, M. J. Rosseinsky, D. W. Murphy, and R. C. Haddon, Phys. Rev. Lett. **69**, 1687 (1992).
[23] K. Allen and F. Hellman, Phys. Rev. B **60**, 11765 (1999).
[24] See Supplemental Material for further details.
[25] W. P. Beyermann, M. F. Hundley, and J. D. Thompson, Phys. Rev. Lett.

68, 2046 (1992).
[26] R. H. Zadik *et al.*, in preparation.
[27] F. Bouquet *et al.*, Europhys. Lett. **56**, 856 (2001).
[28] N. P. Raju, E. Gmelin, and R. K. Kremer, Phys. Rev. B 46, 5405 (1992).
[29] J. A. Eisele and F. Keffer, Phys. Rev. 96, 929 (1954).
[30] S. Kawasaki *et al.*, J. Phys. Soc. Jpn. **82**, 014709 (2013).
[31] E. Shender, Sov. Phys. JETP **56**, 178 (1982).
[32] T. Yildirim, A. B. Harris, E. F. Shender, Phys. Rev. B **58**, 3144 (1998).
[33] E. V. Kuz'min, J. Exp. Theor. Phys. **96**, 129 (2003).
[34] M. A. de Vries, A. C. Mclaughlin, and J.-W. G. Bos, Phys. Rev. Lett. **104**, 177202 (2010).
[35] H. Shinaoka, Y. Tomita, and Y. Motome, Phys. Rev. Lett. **107**, 047204 (2011).
[36] S. Satpathy *et al.*, Phys. Rev. B **46**, 1773 (1992).
[37] D. A. Huse and V. Elser, Phys. Rev. Lett. **60**, 2531 (1988).
[38] K. Kanoda and R. Kato, Annu. Rev. Condens. Matter Phys. **2**, 167 (2011).

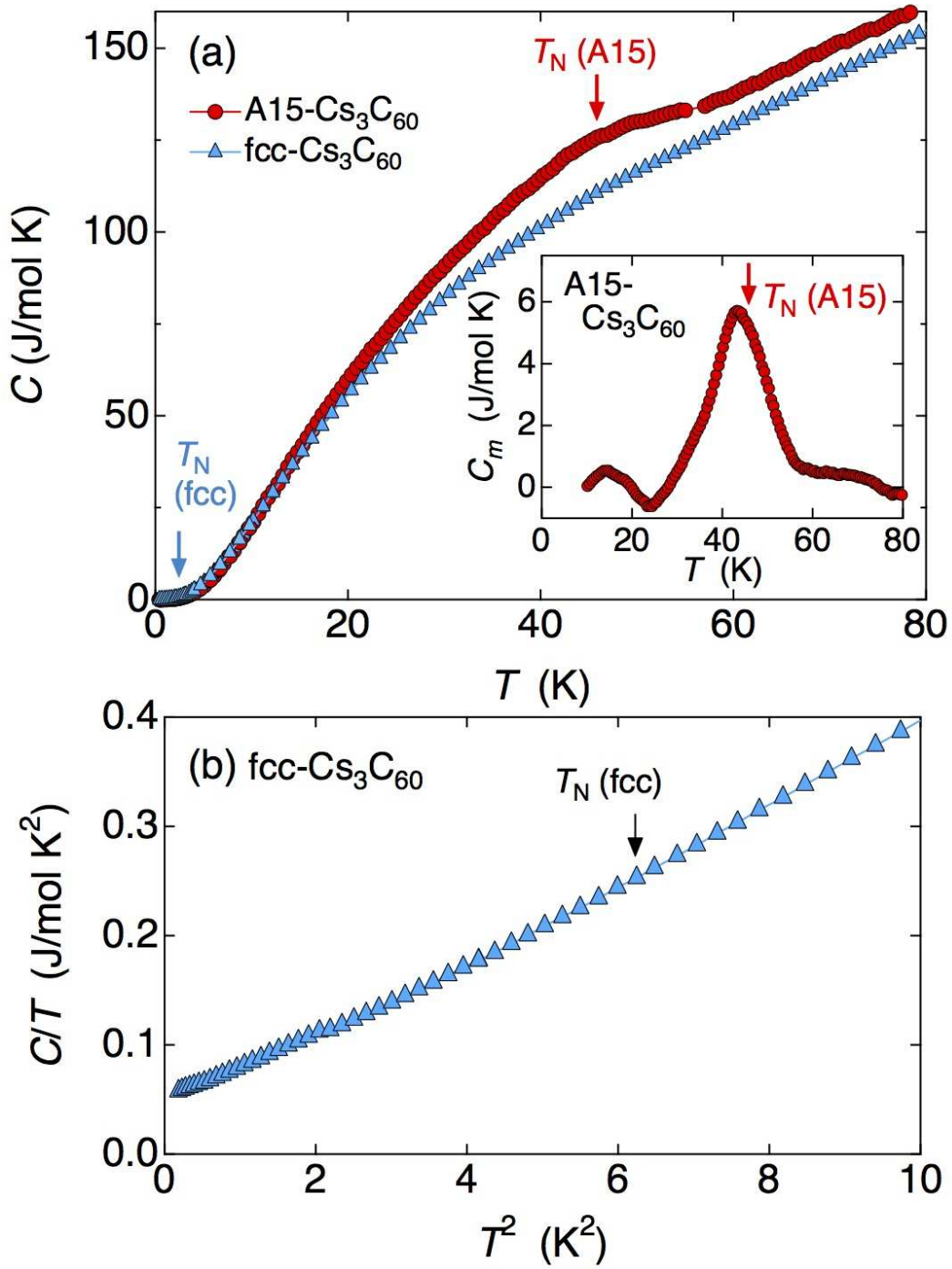

FIG. 1. (Color online) (a) Main panel: Temperature dependence of the specific heat, C, for fcc- and A15-Cs_3C_{60} (triangles and circles, respectively). Inset: Temperature dependence of the magnetic specific heat, C_m, for A15-Cs_3C_{60} obtained by subtracting the phonon background contributions from total C. (b) Low temperature part of C/T for fcc-Cs_3C_{60}, plotted as a function of T^2.

Arrows indicate the reported Neel temperature T_N = 2.2 K and 46 K in fcc- and A15-Cs_3C_{60}, respectively.

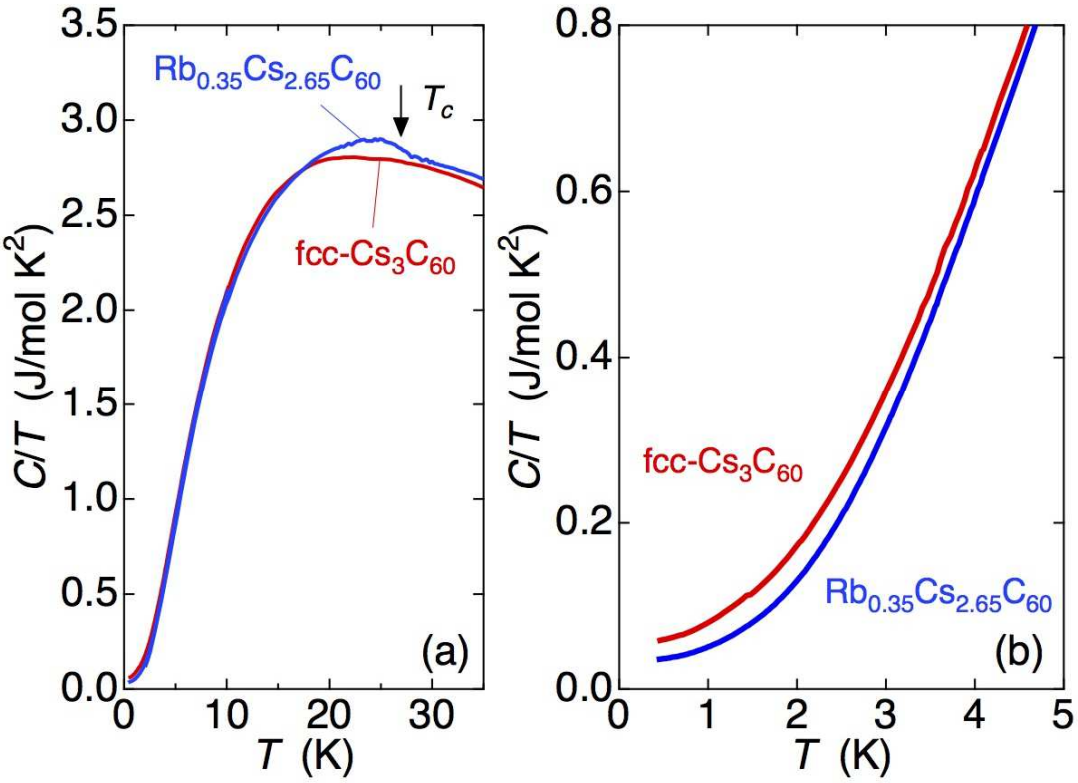

FIG. 2. (Color online) Temperature dependence of the specific heat, $C/T(T)$, for antiferromagnetic fcc-Cs_3C_{60} and superconducting $Rb_{0.35}Cs_{2.65}C_{60}$, below (a) 35 K and (b) 5 K, respectively. Arrow indicates the superconducting transition temperature $T_c = 27$ K for $Rb_{0.35}Cs_{2.65}C_{60}$.

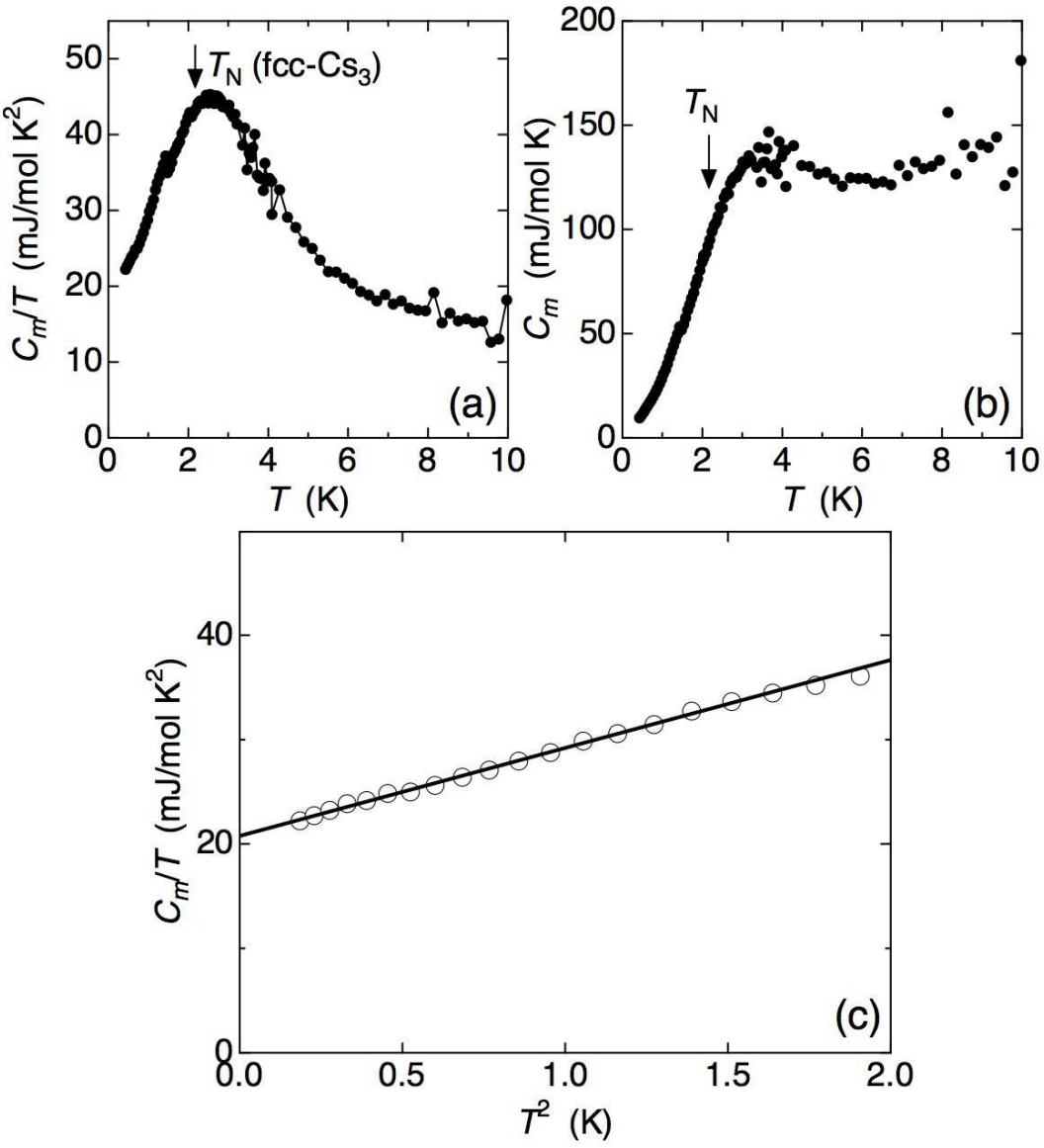

FIG. 3. (Color online) (a) The magnetic specific heat divided by temperature, C_m/T, as a function of temperature. C_m was obtained by subtracting C for superconducting $Rb_{0.35}Cs_{2.65}C_{60}$ from C for fcc-Cs_3C_{60}. (b) C_m plotted as a function of T. (c) C_m/T plotted as a function of T^2. Solid line is a linear fit. Arrows represent the reported T_N.

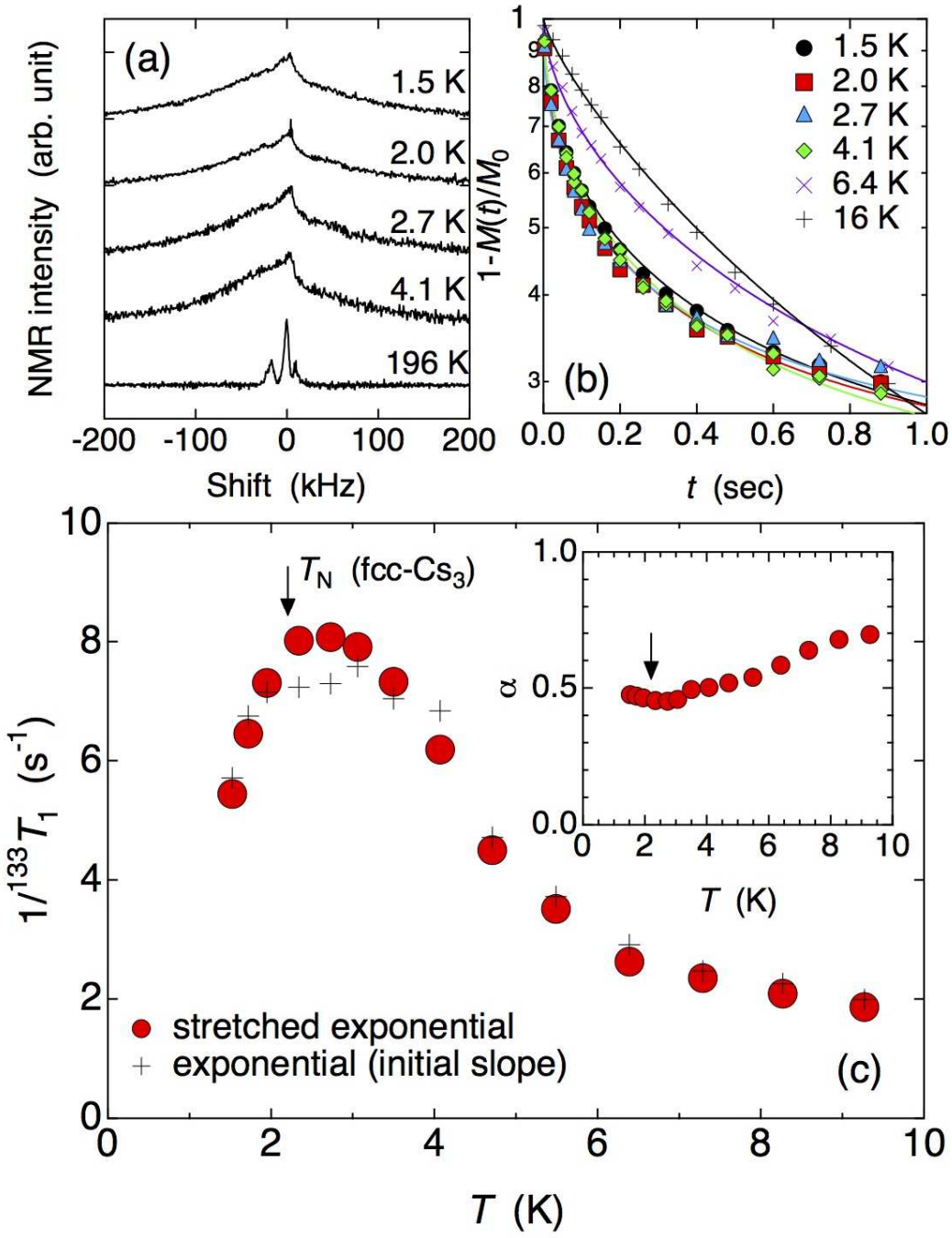

FIG. 4. (Color online) (a) Temperature evolution of ^{133}Cs NMR spectrum in fcc-Cs_3C_{60} measured at H = 8.0018 T. (b) Temperature dependence of the nuclear magnetization decay curves for the fast relaxing component. Solid curves are the fits assuming the stretched exponential decay, $1 - M(t)/M_0 \propto \exp[-(t/T_1)^{\alpha}]$, where α, M_0, and $M(t)$ are a stretch exponent, the nuclear magnetizations in the thermal equilibrium and a time t after saturation

comb pulses, respectively. (c) Temperature dependence of $1/^{133}T_1$. The solid circles (crosses) were obtained by the fits using the stretched exponential model (simple exponential model). Inset: Temperature dependence of the stretch exponent for the fast relaxing component. Arrows indicate $T_N = 2.2$ K.

Word count:

PRL limit (main body, figure, caption, footnotes) 3,500 words

Main body: 2,374 words
Figure captions: 212 words
Total: 2,586

Space for Figures : 3,500-2,586 = 914