Mott Transition in the A15 Phase of Cs$_3$C$_{60}$: Absence of a Pseudogap and Charge Order


Laboratoire de Physique des Solides, CNRS, Université Paris-Sud, Université Paris-Saclay, 91405 Orsay, France
CNISM and Dipartimento di Fisica, Università di Parma—Via G.P. Usberti 7/a, 43100 Parma, Italy
Department of Physics, University of Helsinki, Gustaf Hällström katu 2a, P.O. Box 64, 00014 Helsinki, Finland
Synchrotron SOLEIL, Orme des Merisiers, Saint-Aubin, B.P. 48, 91192 Gif-sur-Yvette Cedex, France

We present a detailed NMR study of the insulator-to-metal transition induced by an applied pressure $p$ in the A15 phase of Cs$_3$C$_{60}$. We evidence that the insulating antiferromagnetic (AFM) and superconducting (SC) phases coexist only in a narrow $p$ range. At fixed $p$, in the metallic state above the SC transition $T_c$, the $^{133}$Cs and $^{13}$C NMR spin-lattice relaxation data are seemingly governed by a pseudogaplike feature. We prove that this feature, also seen in the $^{133}$Cs NMR shift data, is rather a signature of the Mott transition which broadens and smears out progressively for increasing $(p,T)$. The analysis of the variation of the quadrupole splitting $\nu_Q$ of the $^{133}$Cs NMR spectrum precludes any cell symmetry change at the Mott transition and only monitors a weak variation of the lattice parameter. These results open an opportunity to consider theoretically the Mott transition in a multiorbital three-dimensional system well beyond its critical point.

DOI: 10.1103/PhysRevLett.118.237601

In the cuprates, a Mott antiferromagnetic (AFM) insulating state is driven into a superconducting (SC) state by a chemically induced increase of the carrier content. Another paradigm for correlated electron systems is to induce such a change of electronic state by an applied pressure $p$ [1,2]. An experimental realization requires a material with a large on-site Coulomb repulsion $U$ to stabilize an insulating state at ambient $p$. A significant compressibility is then required to permit an increase with $p$ of the bandwidth $W$, allowing one to span a large range of $U/W$ values. Because of these restrictions, only a few compounds exhibit such an ideal Mott transition.

The most investigated compounds so far have been the vanadium oxides which exhibit a metal-to-insulator transition (MIT) above room $T$, though towards non-SC ground states. As for many other cases studied, a change in the atomic structure often occurs at the MIT, as, for instance, in doped VO$_2$, which displays a spin-Peierls transition concomitant to the MIT [3]. On the contrary, V$_2$O$_3$ undergoes a MIT [4,5], which has been considered as a prototypical case since the 1960s. It has been mostly studied in samples with slight Cr or Ti substitution on the V site that induces doping but also an uncontrolled amount of disorder. This yields an inhomogeneous phase coexistence range near the MIT [6].

Recently, original Mott transitions towards a SC ground state have been revealed in organic materials either of the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) family [7,8] or in the fulleride compound Cs$_3$C$_{60}$ [9,10]. Such compounds are highly compressible, as the bindings between the organic or fullerene molecules occur through van der Waals interactions. In the case of Cs$_3$C$_{60}$, detailed studies of the electronic properties have been limited, as actual samples are air-sensitive powders, often multiphased. However, NMR experiments permitted one to establish that a MIT occurs in both isomorphic cubic forms of this compound. The A15 phase exhibits a transition from a Néel AFM to a SC metal with increasing $p$, while the fcc phase evolves from a frustrated magnetic state to a SC state [10,11]. Recent low-$T$ experiments on a well-controlled nearly A15-pure sample permitted us [12] a thorough study of the SC state properties on the high-$p$ side of the Mott transition.

On this improved sample, we evidence here that the AFM-SC phase coexistence range at the Mott transition is rather small. We furthermore show that at fixed $p$ the thermal lattice expansion drives a transition between paramagnetic metal (PM) and insulating (PI) states, as reported for the organic conductor [8] and as was suggested [13] for the fulleride compound Na$_2$CsC$_{60}$. From NMR data taken on multiphased samples, we did initially suggest that such a transition occurs as well in the fcc Cs$_3$C$_{60}$ [14]. Here the much higher experimental accuracy permits us to reveal the absence of a pseudogap, which differentiates the fullerides from the cuprates near their respective Mott transitions.

We further demonstrate that, at variance with the organic compounds, the slope $dp/dT$ of the MIT remains positive over the whole phase diagram. Finally, the $^{133}$Cs NMR quadrupolar splitting $\nu_Q$ reveals only a small step variation of the lattice parameter at the Mott transition. The increase at high pressure of the apparent width of the transition suggests a possible location of the critical point $p_c$ in the phase diagram and allows us to compare the continuation of the Mott transition to a Widom line [15–17]. These results should also allow one to consider theoretically the incidence of
multiorbital [18] and Jahn-Teller [19,20] effects detected in these compounds.

Mott transition and low-T AFM-SC coexistence.—We present here a detailed investigation of the T variation of the $^{133}$Cs NMR spectra at low $p$ in the pure Mott-AFM phase and for $p > p_c \sim 5$ kbar for which the SC state is fully established [12]. The $^{133}$Cs NMR spectra exhibit a similar quadrupole splitting (for $I = 7/2$) in both paramagnetic regimes, but their shifts and width differ in the AFM and SC states (see [21], Sec. I). This permitted us to evaluate at a given $p$ the AFM phase content from the signal loss occurring in the AFM state in a specific frequency window of the NMR spectrum, as detailed in Sec. I of Ref. [21]. As displayed in Fig. 1(a), the loss onsets below $T_N \sim 47$ K for all pressures $p < 5.4$ kbar, while it onsets only at $T_c \sim 35$ K for $p \geq 5.9$ kbar. Therefore, the magnetic and metallic states coexist only on a narrow $p$ range with a quasiconstant Néel temperature. The comparison of the local NMR data on the magnetic state with the SC fraction taken on the macroscopic diamagnetic data is displayed in Fig. 1(b). It establishes that, up to $T = 50$ K, the transition occurs at the nearly $T$-independent pressure $p_{c0} = 5.1 \pm 0.3$ kbar. The sharpness of this transition with a small $p$ extension $\Delta p/p_c = \pm 6\%$ of the coexistence regime is good evidence for the expected first-order character of the Mott transition.

Pseudogaplike variation of the NMR spin-lattice relaxation $T_1$ in the metallic state.—To follow the evolution of the electronic properties toward high $T$ in the metallic state, we have first taken $T_1$ data on both $^{13}$C and $^{133}$Cs for a chosen pressure of 5.9 kbar, for which the sample is fully in the metallic state at low $T$. In the paramagnetic state, the nuclear magnetization recovery was found to exhibit a stretched exponential behavior $M(t)/M_0 = \exp[-(t/T_1)\beta]$, with an identical exponent value $\beta = 0.85(5)$ ($\beta$ did only slightly vary below $T_N$ and $T_c$ [12]). The large decrease of $(T_1 T)^{-1}$ due to the opening of the SC gap is clearly evidenced in Fig. 2(a). There, one can see as well a large steplike increase for $T > 80$ K which is found to scale quite well for the two nuclear spin species. Being here very near to the Mott transition, one might consider that, in analogy to the case of underdoped cuprates, an incomplete pseudogap [27] opens and is followed by a full SC gap opening at lower $T$. However, for a wave-vector-dependent pseudogap due to AFM fluctuations, distinct $T$ dependences of $T_1$ should occur for the two nuclear spin species, as $^{13}$C resides on the magnetic $C_{60}$ molecules (cf. $^{63}$Cu in cuprates [28,29]), while $^{133}$Cs, being located in a symmetric position in the AFM lattice, would hardly sense the AFM fluctuations (cf. $^{89}$Y or $^{17}$O in cuprates [27]).

Recovery of the insulating state at high $T$.—Such a pseudogap being ruled out by these data, we shall see hereafter that $^{133}$Cs $T_1$ and NMR shift data for a series of pressures above and below $p_{c0}$ do allow us to establish that the high-$T$ transition corresponds to the restoration of a PI state.

(i) Paramagnetic state spin-lattice relaxation.—In Fig. 2(b), we report first former 1 bar data [10] taken on a large $T$ range on distinct samples sealed in glass capillaries. There we recognize the large increase of $(T_1 T)^{-1}$ with decreasing $T$ [10,11], followed by a sharp decrease due to the opening of the magnetic gap in the AFM state below $T_N = 47$ K. In the PI state, this variation corresponds to a Curie-Weiss-like behavior $(T_1 T)^{-1} = B/(T + \theta)$ with $\theta = 60 \pm 5$ K, of the order of magnitude of $T_N$ as expected for a dense paramagnet [10,11]. In Fig. 2(b), we report then a series of $(T_1 T)^{-1}$ data for $p > 2$ kbar taken on the sample housed in the pressure cell. Below 4.7 kbar, they exhibit convex $T$ dependences similar to that seen on the 1 bar samples. The small 20% magnitude deviation could be mainly assigned to sample and NMR
probe differences in the two experimental setups. For all pressures \( p > 5.1 \) kbar, we see that the formerly studied [12] SC state increase of \((T_1T)^{-1}\) up to \(T_c\) is followed by a second steplike increase as that seen in Fig. 2(a). This is evidenced by the inflection point and the concave variation displayed by all the data curves. One might notice that, at higher \( T \) values, \((T_1T)^{-1}\) recovers a decreasing behavior strikingly identical to that seen for the PI state at 4.1 kbar. This ascertains that the step increase of \((T_1T)^{-1}\) indeed locates the MIT. For \( p \geq 7.8 \) kbar, an intermediate plateau of \((T_1T)^{-1}\) suggestive of a PM Korringa behavior [30] can be noticed between the two regimes. (ii) NMR shifts from the \(^{133}\)Cs NMR spectra.—The transition from a PM to a PI can be detected as well on the electronic spin susceptibility, which can be monitored from the \(^{133}\)Cs NMR shift. With a single \( I = 7/2 \) Cs nuclear spin site, the spectra could be fitted as exemplified in Sec. II of Ref. [21] to deduce the NMR shift tensor, the quadrupole frequency \( \nu_Q\), and its asymmetry parameter \( \eta \). For all pressures below 11 kbar, the isotropic contribution \( K_{iso} \) to the NMR shift increases with \( T \) as shown in Fig. 3(a). The data presented above permitted one to detect only an overall variation of the lattice parameter [9]. We also took x-ray data, described in Sec. III of Ref. [21], which allows us to confirm that the A15 lattice cell symmetry is not subsequently modified from the Mott state up to \( p = 11 \) kbar. The nuclear quadrupole frequency \( \nu_Q \) deduced from the \(^{133}\)Cs NMR spectra is also directly related to the distribution of charges and then to the atomic structure and the ordering of the \( C_{60} \) molecular orbitals. The extensive spectral fits described in Ref. [21] permitted us to determine the \( T \) variations of \( \nu_Q \) shown in Fig. 3(b). Those are naturally found quite smooth in the absence of any crossing of the MIT for \( p < 4.7 \) kbar. However, for \( 5.1 < p < 7 \) kbar, minute step decreases of \( \nu_Q \) with increasing \( T \) are evidenced near the transition temperatures detected from the \( T_1 \) and \( K_{iso} \) data of Figs. 2(b) and 3(a). No such signature of the transition could be detected at higher \( p \). We recall that \( \nu_Q \) gives a measure of the electric field gradient (EFG) on the Cs atomic site with \( \nu_Q \propto d^2V/dr^2 \), where \( V(r) \) is the potential around the Cs site located at \( r = 0 \). As \( V(r) \) has dimension \( L^{-1}, \nu_Q \) has dimension \( L^{-3} \). Assuming a uniform lattice contraction with increasing \( p \), this dimensional analysis demonstrates that one roughly expects \( \nu_Q \propto \alpha^{-3} = 1/v \), where \( v \) is the lattice unit cell volume. We shall consider first the qualitative information gained on the phase diagram from the \( \nu_Q \) data, while a quantitative analysis of the variation of lattice parameter will be attempted later. Phase diagram.—The data presented above permitted us to evidence on \((T_1T)^{-1}, K_{iso}\), and \( \nu_Q \) that the metallic state crosses over toward the insulating state with increasing \( T \) at a given \( p \). We are now able to discuss the main characteristics of the transition line \( T_{MIT}(p) \) and its apparent width. (i) Transition line.—We already know from the discussion done on the AFM-SC fractions that the transition line is nearly vertical at \( p = 5.1 \) kbar, from \( T = 0 \) to 50 K. For higher \( p \), the temperature \( T_Q \) at which a small step decrease of \( \nu_Q \) is detected permits one to locate the evolution of the transition up to \( p \sim 6.4 \) kbar. The magnetic responses \((T_1T)^{-1}\) and \( K_{iso}\), which scale with each other in the metallic regime (see [21], Sec. II), give a determination of the transition which can be followed at larger \( p \). The maximum of \((T_1T)^{-1}\) marks the full restoration of the insulating state that is the upper limit \( T_{max} \) for the MIT. One might as well assign a width to the transition and consider that the MIT sits at the inflection point \( T_{mid(T_1)} \) of \((T_1T)^{-1}\) versus \( T \) (or equivalently \( T_{mid(K)} \) for \( K_{iso} \) versus \( T \)), which can be obtained by fitting the fixed \( p \) data with a steplike function with a half intensity width \( \Delta_T \), as done in Sec. II of Ref. [21]. The data for \( T_{max}, T_Q, T_{mid(T_1)} \), and \( T_{mid(K)} \) plotted in Fig. 4 give therefore a good representation of the variation of the MIT, which bends over for increasing \( p \) in the actual phase diagram. In the fcc Cs\(_{60}\) phase, a similar MIT transition line has been suggested solely from NMR \( T_1 \) data taken with increasing pressure (Figs. 5 and 6 of Ref. [14]) or for Rb-substituted samples [20].
at \( T = 14.5 \text{ K} \) correspond to an initial linear \( p \) dependence of the lattice cell volume \( \Delta V / \nu dp = -6.2 \times 10^{-3} / \text{kbar} \). From Fig. 3(b), we obtain \( \nu Q dp = 0.02 / \text{kbar} \) for \( p < 5 \text{ kbar} \) at a fixed \( T \) of 50 (or 80) K for which the sample remains in the PI state. Therefore, \( \nu Q \) exhibits a 3 times faster increase with unit cell contraction than expected. While this limits the significance of the model, we may consider that this experimental scaling can be applied as well for the \( \approx 1 \text{ kHz} \) decrease of \( \nu Q \) at the MIT. That would correspond to about \( \delta \nu / \nu = 0.008 \), that is, an increase of lattice parameter \( da/a \approx 2 \times 10^{-3} \), which is within the error bar of the synchrotron x-ray data we have collected so far in diamond anvil cells [21].

Let us recall here that \( \nu Q \) involves two contributions \( \nu Q = \nu Q,i + \nu Q,b \). The first one, associated with the EFG created by large distance ions, is correctly estimated within the above model. The second contribution is due to the ionic charges and electrons distributed in the Cs first-nearest neighbor molecular \( C_{60} \) orbitals. In the absence of a modification of the \( C_{60} \) ball diameter with \( p \) and \( T \) (confirmed in Ref. [21], Sec. III), the unit cell does not contract uniformly. This might essentially control the local contribution \( \nu Q,b \) associated with the \( C_{60} \) molecular orbitals, which could as well be sensitive to the appearance of extended states at the Mott transition.

**Conclusion.**—We have shown here that \( A_{15} \text{ Cs}_5 C_{60} \) presents a quasi-ideal Mott transition and performed an NMR study which allowed us to reveal the absence of a pseudogap and charge order near the Mott transition. This lack of competing order might explain that \( T_c \) remains quite high up to the MIT, conversely to the case of hole-doped cuprates. We could establish altogether the evolution of the MIT first-order line in the \( (p, T) \) phase diagram towards a continuous transition. Quite remarkably, we also find that the insulating state restored from the metallic state by the thermal expansion of the lattice has magnetic properties quite analogous to those found at high \( T \) in the pure insulating Mott state. This might indicate that quantum fluctuations do govern the continuous transition at high \( (p, T) \), which therefore differs from the Widom line occurring in classical systems, e.g., the liquid-gas transition. Let us recall as well that the maximum of \( (T_1 T)^{-1} \) versus \( T \), which has been revealed for some time [31], in the dense \( A_3 C_{60} \) light-alkali compounds is quite similar to that detected here above \( p = 7.8 \text{ kbar} \). This gives a strong hint that in all these compounds the maximum of \( (T_1 T)^{-1} \) represents the crossover towards the local moment behavior of the PI state. Finally, contrary to the case of the organic triangular lattice crystals, the critical line has a positive slope with respect to \( p \). This entropy-related slope, which suggests higher entropy in the insulating state linked with orbital degeneracy, qualitatively agrees with the results of dynamical mean field theory (DMFT) calculations for fcc \( A_3 C_{60} (A = K, Rb, Cs) \) [18]. More quantitative simulations taking into account the \( A_{15} A_3 C_{60} \) lattice geometry could
permit one to investigate the interplay between orbital and spin degrees of freedom in this genuine Mott transition.

We acknowledge Synchrotron-SOLEIL for providing beam time and thank S. Ravy for assistance in taking x-ray data on the CRISTAL beam line (Projects No. 2010286 and No. 20110678). We also have had stimulating discussions with S. Biermann, Y. Nomura, V. Dobrosavljevic, and M. Rozenberg.

[21] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.118.237601, which includes Refs. [22–26], for the analysis of the AFM fraction near the MIT from the $^{133}$Cs NMR spectra, in section I. The quadrupole frequency $\nu_Q$ and the NMR shift data in the paramagnetic state are deduced from the detailed spectral fits of the $^{133}$Cs NMR spectra in section II. The latter are compared with the $(T_1T)^{-1}$ data. In section III the x-ray spectra for three different pressures are reported and the deduced temperature variations of the lattice parameter are discussed.