

Electronic properties of the $\text{Na}_2\text{AC}_{60}$ family ($\text{A}=\text{K}, \text{Rb}, \text{Cs}$)

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Electron Spin Resonance (ESR) at ambient and under high pressure and optical reflectivity measurements were used to study the consecutive phase transitions in $\text{Na}_2\text{AC}_{60}$ family of fulleride compounds. The high temperature *fcc* phase in all three $\text{A}=\text{K}, \text{Rb}, \text{Cs}$ compounds are found to show *semi-metallic* behaviour. For the first time a peculiar sequence of phase transitions from *semi-metallic* to *metallic* to *superconducting* phases are observed in $\text{Na}_2\text{CsC}_{60}$. The metallic properties of the polymeric phases in $\text{A}=\text{K}, \text{Rb}$ were established.

INTRODUCTION

The steeper dependence of superconducting transition temperature T_c on the lattice constant in $\text{Na}_2\text{AC}_{60}$ compounds¹ with respect to other (not Li or Na based) $\text{A}_2\text{A}'\text{C}_{60}$ ($\text{A}, \text{A}'=\text{K}, \text{Rb}, \text{Cs}$) or A_3C_{60} ($\text{A}=\text{K}, \text{Rb}$) compounds has still not been satisfactorily explained. It is experimentally well established from both physical and chemical pressure studies that the variation of T_c is related to the change in the density of states at the Fermi level, $N(\epsilon_F)$. Therefore, a different dependence of $N(\epsilon_F)$ on the lattice constant a is expected for $\text{Na}_2\text{AC}_{60}$ compounds. The low temperature phase of $\text{Na}_2\text{AC}_{60}$ is *sc* with orientational order^{2,3} in contrast to the merohedrally disordered *fcc* phase of the $\text{A}_2\text{A}'\text{C}_{60}$ compounds. This is ascribed to the smaller size of Na that promotes a configuration where the nearest possible distance between C atoms on adjacent C_{60} balls is achieved. Based on the different structure of $\text{Na}_2\text{AC}_{60}$ compounds it was argued that modified electron hopping is responsible for the different variation of $N(\epsilon_F)$ with a . It has to be pointed out that in their early work Maniwa et al.⁴ indeed found a scaling of T_c with locally measured $N(\epsilon_F)$ in $\text{Na}_2(\text{K},$

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Rb)C₆₀ but the values are deduced in the temperature range where a polymer phase is also present, at the time yet unknown. No evidence for a different variation of $N(\epsilon_F)$ on a is found in Na₂CsC₆₀ and K₃C₆₀ or Rb₃C₆₀ in the work of Tanigaki et. al.⁵. Most probably it is the single electron band model which fails to explain for all experimental observations. As already mentioned Na₂(K, Rb)C₆₀ undergoes polymerization below 250 K at ambient pressure⁶ whereas Na₂CsC₆₀ polymerizes only under pressure⁷. In contrast to the doubly bonded A₁C₆₀ polymers⁸, Na₂AC₆₀ polymer forms single bonds. In this work we present a comprehensive study of the physical properties of Na₂AC₆₀ compounds in all their three structural phases. We show that the *sc* and the *polymer* phases are metallic, whereas the high temperature *fcc* phase shows a *semi-metallic* behaviour, adding a new phase to the already very rich phase diagram of C₆₀ fullerides. We discuss how the observation of this phase might be linked to the peculiar properties of Na₂AC₆₀ compounds.

EXPERIMENTAL

Samples were prepared by conventional solid-state reaction method. Phase purity was checked by X-ray diffraction. ESR experiments were performed on commercial ESR spectrometer and cavities in X-band (at 9.5 GHz) in the temperature range of 5 to 800 K. ESR intensities were thoroughly calibrated by CuSO₄ · 5H₂O reference samples and also all experimental conditions were monitored in the full temperature range for a reliable measure of the spin-susceptibility. When studying polymerization, slow cooling rate was imposed (typically 50 K/hour). Quenching was done by immersing the sample from room temperature into liquid nitrogen and putting it in the precooled ESR cryostat, immediately. High pressure ESR studies were performed up to 5 kbar. The infrared reflectivity measurements were performed up to 14000 cm⁻¹ in a sealed sample holder with a wedged diamond window described in Ref. 9.

RESULTS AND DISCUSSION

Polymerization in Na₂KC₆₀ and Na₂RbC₆₀

At room temperature the ESR signal of Na₂RbC₆₀ consists of single relaxationally broadened line with a linewidth of 4 mT. This is the conducting ESR(CESR) signal of the metallic simple cubic (*sc*) phase. As shown in Fig. 1a. when the sample is slowly cooled below 250 K a new line appears with a linewidth of 0.5 mT. Similar signals are observed in Na₂KC₆₀ with the only difference in the linewidths (1.2 mT and 0.2 mT for the signal of the room temperature *sc* phase and for the new signal appearing below 250 K, respectively) that is due to the scaling in the CESR relaxation rates which are dominated by the spin-orbit coupling on the alkali (Rb or K). Since this temperature range coincides with the appearance of the *polymer* phase we associate the new signal with that of the *polymer*. Fig. 1b. and 1c. show the intensities and linewidths of the two lines after deconvolution into two derivative Lorentzian lines.

The broader signal corresponds to the *sc* phase while the narrow component to the *polymer*. Unless quenched, $\text{Na}_2\text{KC}_{60}$ was always found to fully polymerize below 200 K whereas polymerization is only partial even for slow cooling for $\text{Na}_2\text{RbC}_{60}$. In the temperature range of 250-200 K intensity of the ESR signal of the *polymer* increases. The signal of the *sc* phase drops at the same time with an amount equal to the increase in the intensity of the *polymer* phase. Therefore the susceptibility of the *polymer* phase is equal to that of the *sc* that is $3 \cdot 10^{-4}$ emu/mol. The *polymer* fraction saturates at 200 K at a ratio of 1:4 *polymer*/cubic. Significantly reduced cooling rate did not enhance polymerization. Hysteresis is observed in the *polymer* fraction in agreement with hysteretic lattice constant data¹⁰. Hysteresis is explained by macroscopic strains in the *polymer* phase. In the temperature range where polymerization is completed, for both compounds the *polymer* phase shows a simple metallic susceptibility and for $\text{Na}_2\text{RbC}_{60}$ the still present *sc* phase is also a metal. Below 50 K susceptibility of the *polymer* appears to increase, an effect explained by an impurity phase which linewidth and *g* factor are close to that of the *polymer*. This impurity phase was also found in quenched experiments where the *polymer* was not present. X-band ESR technique is limited at this point and NMR or high-field ESR is required for the study of the single bonded *polymer* below 50 K. ESR linewidth of Fig. 1c. shows a clear linear, i.e. phonon dominated, relaxation mechanism of both phases. The slight up-turn of the linewidth of the *polymer* is an effect of the impurity phases. The smaller ESR linewidth of the *polymer* implies that the electronic wave functions in this phase overlap less with the alkali than that of the *sc* phase.

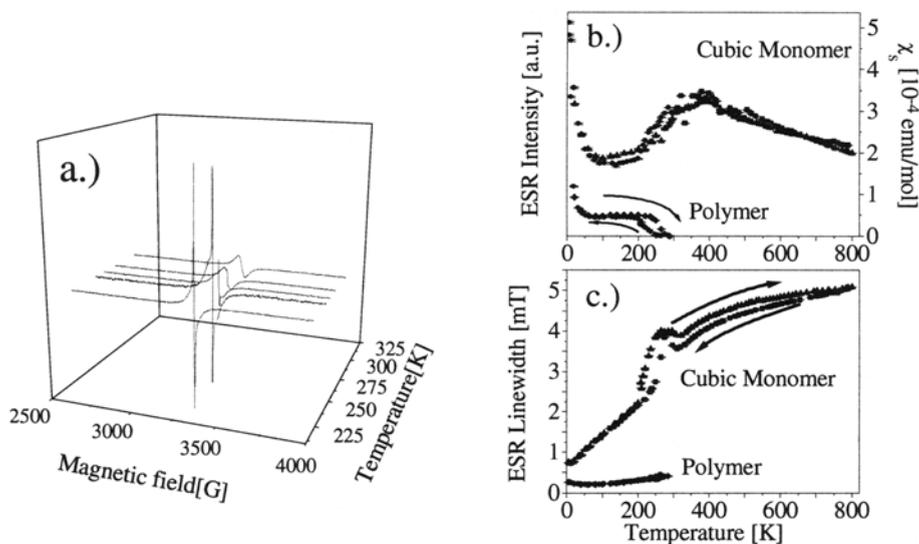


FIGURE 1a. The emerging line in the ESR signal of $\text{Na}_2\text{RbC}_{60}$ below 250 K is from the *polymer* phase. Due to its longer relaxation rate i.e. higher relative *amplitude* the new line dominates the ESR signal. Fig. 1b. and Fig. 1c. show intensity and linewidth of ESR lines. The right hand scale of Fig. 2a shows the spin-susceptibility of the signal normalized by the full amount of sample. It gives a measure of the spin-susceptibility in the presence of one line only.

In Fig. 2. polymerization is shown under pressure for $\text{Na}_2\text{KC}_{60}$. The linewidth for both phases shows a decrease in agreement with a model of a 3D metal by Elliot¹¹. This variation of the linewidth of the *polymer* phase can be contrasted to the behaviour in A_1C_{60} *polymers* where the linewidth *increases* under pressure implying a 1D electronic properties¹².

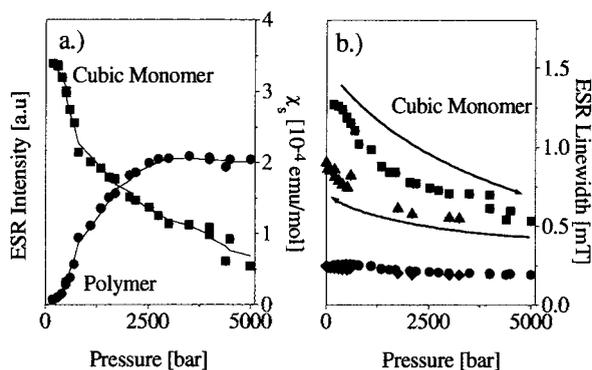


FIGURE 2. High pressure induced polymerization in $\text{Na}_2\text{KC}_{60}$ at ambient temperature (295 K). Solid lines are guides to the eye. Arrows indicate the direction of pressure change. Linewidth of the cubic phase shows hysteresis.

High temperature *fcc* phase in $\text{Na}_2(\text{K, Rb and Cs})\text{C}_{60}$

As is shown in Fig. 1c. the *sc-fcc* phase transition around room temperature can be traced in the ESR spectra as an extremum in the linewidth. The temperature of the extremum (310 K) is close to the value found by Tanigaki et al.² (313 K) in DSC studies for $\text{Na}_2\text{RbC}_{60}$. Above this transition temperature linewidth shows a non-linear temperature dependence. Also hysteresis in the linewidth is observed after the 800 K heat treatment. For all three compounds through the *sc-fcc* transition temperatures the spin-susceptibility changes continuously with a gradual drop that is most significant for $\text{Na}_2\text{CsC}_{60}$ (not shown), where the spin-susceptibility drops a factor of 2 in the temperature range of 300-800 K. The temperature dependence of the spin-susceptibility variation resembles a Curie-like dependence, although from the Curie constant we obtain only 1/7 spins per C_{60} units. The situation therefore is not at all analogous to the case of CsC_{60} where in its high temperature *monomer* phase the Curie-like susceptibility corresponds to one spin per C_{60} ¹³. Apart from localization, other models like change in the density of states due to lattice expansion or assuming the development of a spin-gap for the conducting electrons would give just the opposite trend in the temperature dependence of the spin-susceptibility. In the *fcc* phase the ESR linewidth is still large therefore spins are not localized on C_{60} balls. To further clarify the nature of this high temperature *fcc* phase we performed IR reflectivity studies. Based on our preliminary results, a *metal to insulator*

transition(MIT) is found through the *sc-fcc* phase transition those nature is discussed in more detail in Ref. 9. All these observations point toward a picture where the experimental results in the *fcc* phase are not explained by a single electron model but electron-electron correlations should be taken into account. This *semi-metallic* phase is believed to arise as a results of close criticality to a MIT due to strong correlation effects. Most probably Anderson-like disorder, due to the free tumbling of Jahn-Teller distorted C_{60} balls, also plays an important role in determining the physical properties. Additional theoretical work is required to further elucidate the nature of this high temperature phase to coherently explain all the observations. We believe that this close proximity to a non-metallic phase is inherited into the low temperature *sc* phase that would explain the difference in response of T_c to the lattice parameter between the *fcc* $A_2A'C_{60}$ and *sc* Na_2AC_{60} compounds.

CONCLUSIONS

ESR and optical reflectivity measurements have shown: i.) polymerization can be followed in Na_2KC_{60} and Na_2RbC_{60} . Down to low temperatures the polymer remains a metal. Its susceptibility is reminiscent to that of the simple cubic metal. ii.) The high temperature *fcc* phase in all Na_2KC_{60} , Na_2RbC_{60} and Na_2CsC_{60} compounds is shown to be *semi-metallic*. This is believed to be linked to the unique properties of Na_2AC_{60} compounds among other $A_2A'C_{60}$ materials.

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