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CHARACTERIZATION OF KC_{60} OBTAINED VIA
A POTASSIUM CARBONATE ROUTE

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ABSTRACT

KC_{60} synthesized by high temperature annealing of mixture of C_{60} and K_2CO_3 has been characterized by EPR, NMR and differential scanning calorimetry methods. The rich phase diagram with polymeric and dimer phases previously elaborated for KC_{60} is obtained in present work as well. This suggests that alkaline carbonates can be efficiently used in preparation of C_{60} -based polymer materials where C_{60} molecules are charged by alkaline atoms. Another important outcome of present study is that despite high temperatures and presence of oxygen released from K_2CO_3 , EPR and NMR spectra did not exhibit signals which might be referred to fullerene epoxides or related species.

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1. Introduction

Recently considerable attention is given to A_1C_{60} ($A = K, Rb, \text{ and } Cs$) fullerides which demonstrate interesting phase diagrams upon various cooling and heating protocols.¹⁻¹³ The monomeric phase with the fcc rocksalt crystal structure exists in the high temperature region ($T > 500 \text{ K}$).¹⁻³ At slow cooling, it transforms at $T < 400 \text{ K}$ into the phase of the orthorhombic crystal structure^{4,5} where C_{60} molecules are covalently bonded to form polymeric chains.⁵⁻⁷ For KC_{60} , the intermolecular distance in direction of a polymeric chain is $9.11 \text{ \AA}$.^{4,5} The metallic nature of the polymeric phase has been established by temperature-independent spin susceptibility χ_{EPR} in EPR experiments^{4,8} and Korringa law behavior in NMR experiments.⁹ At continuous heating up to about 450 K the polymeric phase returns to the thermodynamically stable high temperature monomeric phase through so-called intermediate phase, which is characterized by the equilibrium state $\alpha-C_{60} + A_3C_{60}$ ($\alpha-C_{60}$ stands for A_xC_{60} with $x \ll 1$).¹⁰ Upon quenching from about 500 K down to $T \leq 270 \text{ K}$, the high temperature monomeric phase transforms into the phase with C_{60} molecules bonded in dimers.^{11,12} For a dimer in KC_{60} , the intermolecular distance is $9.34 \text{ \AA}$.¹¹ The dimer phase has the orthorhombic crystal structure¹² and it is a diamagnetic insulator at low temperatures.¹³ This phase is unstable competing with the polymeric phase and the equilibrium state $\alpha-C_{60} + A_3C_{60}$.^{8,12} With continuous heating the dimer phase transforms sequentially to the monomeric fcc phase then to the polymeric phase and again to the monomeric

fcc phase.⁸ Thus, rich phase diagrams of A_1C_{60} fullerides may suggest broad potentials in variation of characteristics of the C_{60} -based materials.

Alkaline carbonates have been used previously to obtain superconducting fullerides of surprisingly low air-sensitivity.¹⁴ It is natural that they might be likewise applied for producing A_1C_{60} compounds. However, whether by-products of the decomposition of alkaline carbonates will affect polymerization or dimerization processes in A_1C_{60} remained doubtful. One would note that C_{60} and oxygen can form $C_{60}O$ epoxides and $C_{120}O$ dimers.¹⁵⁻¹⁹ $C_{60}O$ is prepared mostly via solution chemistry,¹⁷ but synthesis via solid-state thermal chemistry are mentioned as well.¹⁵ $C_{120}O$ is typically synthesized by heating a solid mixture of C_{60} and $C_{60}O$.¹⁸ On that account, fullerene epoxides and dimers might be expected during the thermal decomposition of alkaline carbonates. Once such species have been appeared, they might influence a unique polymorphism of A_1C_{60} . What makes $C_{60}O$ interesting yet in connection with A_1C_{60} is the same ability to produce polymeric structure.^{18,19} The polymerization of $C_{60}O$ occurs under the electrochemical reduction.^{18,19} Since metal atoms in alkaline fullerides are excellent electron suppliers, the formation of new type polymeric chains, distinct from those of A_1C_{60} , might be considered.

Thus, purposes of present study were twofold. We intended either to prove a particular usefulness of alkaline carbonates for production A_1C_{60} or to point to a new possibility for $[(C_{60})_nO]^{5-}$ species in alkaline fullerides. For this, the mixture of C_{60} and K_2CO_3 , with the stoichiometric ratio to produce KC_{60} , was annealed at

high temperatures in vacuum. The obtained material was examined by EPR, NMR and differential scanning calorimetry (DSC) methods. Specifically, EPR technique has been proven to be exceptionally useful tool in elucidation of phase transitions in KC_{60} .^{4,8,10} On the other hand, considerable quantities of $[\text{C}_{60}\text{O}]^{\delta-}$ and $[\text{C}_{120}\text{O}]^{\delta-}$ species will obviously exhibit distinct EPR spectra^{17,18} and will likely modify the phase diagram of KC_{60} .

2. Experimental

C_{60} (of 99.9% purity) and K_2CO_3 were purchased from Material and Electrochemical Research Corp. (Arizona, USA) and from Sigma Chemical Co. (St. Louis, USA) respectively. K_2CO_3 was dried for 24 hours at 380 K under a dynamic vacuum of about 100 torr. A mixture with a molar ratio of $\text{C}_{60} : \text{K}_2\text{CO}_3 = 1 : 1$ was placed into a quartz tube and heated for 1 hour at 420 K under a dynamic vacuum $\leq 5 \times 10^{-5}$ torr. Afterward, the evacuated tube was sealed out and placed in a furnace for high-temperature treatments from 520 K to 773 K. For EPR measurements samples were prepared in quantities of 10-15 mg in 4 mm diameter tubes, while for DSC and NMR measurements samples were prepared in quantities of about 100 mg in wider tubes. We should note in connection with the preparation procedure that heating in a dynamic vacuum would perhaps completely remove gas products of the reaction. However, the goal of this study is indeed to examine this system under much tightened conditions. Moreover, in a dynamic

vacuum some part of the powder mixture can be forced out from the tube by the gas flow during the decomposition of K_2CO_3 , and this may change the stoichiometric ratio of the final compound.

EPR spectra were measured on an X-band EPR spectrometer Bruker ESP-300E using a 100 kHz modulation frequency. A concentration of spins was determined with reference to that of the 2,2-diphenyl-1-picrylhydazyl (DPPH) sample of known spin content. A g factor was measured with reference to $g = 2.0036$ of DPPH using a Bruker double resonator. A peak-to-peak linewidth (ΔH_{pp}) of the derivative of the EPR absorption was measured with a NMR Gaussmeter Bruker ER035. Low-temperature measurements were carried out with the N_2 gas-flow cryostat.

NMR spectra were recorded with a Bruker MSL-500 (11.7 T) spectrometer at the ^{13}C frequency of 125.5 MHz. A ^{13}C shift of tetramethylsilane was used as a reference for a chemical shift. The temperature was varied within the range 240–360 K.

DSC measurements were performed on a Du Pont 9900 Differential Scanning Calorimeter with the temperature varied over the range 150–500 K with the heating rate 10 K/min. For precaution, the sample was placed into the DSC holder under argon atmosphere in the glove box, despite the fact that KC_{60} is a fairly stable in air.²⁰ The holder was exposed to the ambient atmosphere only for a short time necessary to press-in and transport it into the calorimeter.

3. Results and Discussion.

3.1. Electron Paramagnetic Resonance.

Figure 1 shows evolution of the room temperature EPR spectrum of the mixture of C_{60} and K_2CO_3 with the annealing T gradually increasing from 523 K to 773 K. The sample was annealed for 10 hours at each indicated temperature and slowly cooled down to the room temperature to obtain EPR spectrum.

The sample heated at $T \leq 523$ K demonstrates a single narrow line with $g = 2.0025$ and $\Delta H_{pp} = 1.1$ G (Fig. 1a). An integrated intensity corresponds to the concentration of spins of order of 10^{17} spins per mol. This line is associated with intrinsic, molecular oxygen induced C_{60}^+ radicals²¹⁻²³ and can be essentially reduced in intensity by heating at higher temperatures.²³⁻²⁴ In our experiment its intensity becomes minimal at about 623 K (Fig. 1c), but begins to grow again with further increase in the annealing T (Figs. 1d,e). The growth we relate to additional C_{60}^+ radicals caused by the molecular oxygen released with the decomposition of K_2CO_3 . The $C_{60}O$ epoxide would not show an EPR signal if it is neutral, or would show a signal with g of about 1.997¹⁸ if it is negatively charged by potassium.

The appearance of a much broader signal indicates the formation of the potassium doped C_{60} product (Figs. 1c-f). For the sample heated at 723 K, the broad signal (Fig. 1e) is quite strong, with $g = 2.0006(2)$, $\Delta H_{pp} = 6.5$ G and integrated intensity of three order in magnitude larger than that of the 523 K annealing. However, the strongest EPR signal with $g = 2.0006$, $\Delta H_{pp} = 6.7$ G and with a lesser contribution of the $g = 2.0025$ component is obtained at 773 K

FIG 1 - Evolution of the room temperature EPR spectrum with an increasing annealing temperature for the 1:1 stoichiometric mixture of C_{60} and K_3C_{60} placed into the quartz tube sealed *in-vacuo*. The mixture was annealed at each indicated temperature for 10 hours and slowly cooled down to room temperature to obtain EPR spectrum. An amplifier receiver gain and integrated intensity (in arbitrary units) were as follows: (a) 1×10^6 and 0.324, (b) 1×10^6 and 0.312, (c) 1×10^6 and 1.373, (d) 2.5×10^5 and 17.02, (e) 1×10^5 and 42.36, (f) 1.25×10^4 and 341.88.

(Fig. 1f). Since the EPR spectral shape and parameters did not significantly change with further increase of the annealing T , we dwell on the sample treated at 773 K.

Variation of room temperature EPR parameters upon annealing time at 773 K is presented in Fig. 2, where each experimental point is obtained with the slowly cooled sample. It is remarkable that the concentration of spins reaches its maximal value, of order of 10^{22} spins per mol, after only 30 minutes of the heating (Fig. 2a). The dramatically growth in intensity indicates that the decomposition of K_2CO_3 and process of electron charge transfer from K to C_{60} complete during sufficiently short times. Besides, the polymeric phase is not formed yet since the g factor of 1.9997 (Fig. 2b) is a characteristics of the localized C_{60}^- ion.^{25,26} It needs longer heating times to obtain a homogeneous compound, in which the polymeric phase with a higher g factor can be formed under the slow cooling. In our case, EPR parameters get saturated after about 10 hours and do not apparently change during about 5 days of continuous heating (Fig. 2). Experimental data presented below are obtained with samples synthesized at 773 K for 5 days namely.

First we probe our presumed KC_{60} for the polymer orthorhombic phase which should demonstrate metallic behavior.^{8,10} For this, the sample was re-heated at 573 K for 90 min and slowly cooled down to the ambient temperature. An EPR spectrum with $g = 2.0006$ and $\Delta H_{pp} = 6.9$ G has a Dyson type lineshape, which normally reflects metallic feature (Fig. 3a).²⁷ Another evidence for the polymeric phase we find in a perfect match of our g factor and linewidth with those published for such phase.¹⁰ From the integrated intensity and with the assumption of

FIG 2 - EPR parameters versus time of annealing at fixed temperature 773 K for the 1:1 stoichiometric mixture of C_{60} and K_2CO_3 in the tube sealed *in-vacuo*.

conduction electrons, one may obtain the absolute value of the room temperature spin susceptibility $\chi_{EPR} = 4.6 \times 10^{-4} \text{ emu} \cdot \text{mol}^{-1}$. This value also agrees with the previously reported room temperature spin susceptibility of the polymeric phase of KC_{60} .¹⁰

The sample was then cooled down to 100 K and EPR spectra were taken over the temperature range of 100–400 K with the heating run. The spin susceptibility

FIG 3 - The top plot shows the room temperature EPR spectrum obtained for the slowly cooled sample after annealing at 773 K for 5 days. The spectrum demonstrates the Dyson-type lineshape which normally indicates metallic behavior. The bottom plot shows the spin susceptibility versus temperature. The temperature independent Pauli like χ_{EPR} in the 100-320 K range is the apparent characteristics of the KC_{60} polymeric phase.

shown in Fig. 3b remains constant from 100 K up to about 360 K consistently with the Pauli paramagnetism. This is the strongest conformation of the polymeric orthorhombic phase. A negligible drop in χ_{EPR} at higher temperatures may be the forerunner of the polymeric-to-intermediate phase transition which take place at about 400 K.¹⁰

Figures 4a and 4b show a linewidth and g factor versus temperature respectively. ΔH_{pp} gradually increases from 4.5 G (100 K) to 8.2 G (400 K) while a g factor increases from 2.0001 (100 K) to 2.0006 (400 K). In metals, electron-phonon scattering leads to a linear conductivity $\rho(T)$. In accordance with theory of Elliot²⁸ and Yafet²⁹, there should be a linearity between $\Delta H_{1/2}/\rho$ and Δg^2 , where $\Delta H_{1/2}$ is the halfwidth of the EPR absorption, $\Delta g = g_e - g$ and g_e is a free electron g factor. For conduction electrons this suggests a linear function of temperature for the product $\Delta H_{1/2} \times (\Delta g)^{-2}$. If an EPR lineshape does not change with temperature, then one may replace $\Delta H_{1/2}$ by the experimentally available parameter ΔH_{pp} . Figure 4c shows $\Delta H_{pp} \times (\Delta g)^{-2}$ versus temperature for our sample. Actually, there are two linear regions, from 100 K to about 170 K and from 170 K to 350 K respectively. The turning point at 170 K can be a new feature, but further work is needed to elucidate its possible origin.

Next we examine EPR spectra for phase transitions known for the rapidly cooled (quenched) KC₆₀. The sample was re-heated at 573 K for 90 min, quenched to 77 K by instant immersing into the liquid nitrogen and promptly transferred into the resonator holding at 100 K. EPR spectra were recorded from 100 K to 500 K with the heating run. The variation of χ_{EPR} with temperature is presented in Fig. 5. Fig. 6 shows temperature dependencies of ΔH_{pp} and a g factor respectively.

From 100 K to about 280 K the spin susceptibility of the quenched sample is about four times smaller than that of the slowly cooled sample. Significant decrease in EPR intensity is explained by the formation of dimers in KC₆₀.

FIG 4 - Temperature dependencies of (a) the linewidth, (b) the g factor and (c) the product $\Delta H_{pp} \times (\Delta g)^{-2}$, where $\Delta g = g_e - g$ and g_e is a free electron g factor, measured for the slowly cooled sample of KC_{60} (see text for details).

However, χ_{EPR} does not reach its absolute minimum and shows a weak Curie component (Fig. 5). One may relate this component to the remainder of the monomeric fcc phase since the reduced g factor (1.9996 at 100 K (Fig. 6)) is an attribute of the localized C_{60}^- ions. The possible contribution of the remained K_3C_{60} from the intermediate phase may be much lesser because this stoichiometry

FIG 5 - The spin susceptibility versus temperature (the heating run) for the quenched sample of KC_{60} . In the 100-280 K range KC_{60} is in the dimer phase characterized by minimal χ_{EPR} . In the 280-320 K range the dimerized phase is replaced by the transient monomeric fcc phase, which is followed by the polymeric phase in the 320-380 K range. In the 380-450 K range the polymeric phase changes to the intermediate phase with the phase instability ($\alpha\text{-C}_{60} + \text{K}_3\text{C}_{60}$). Above 450 K the sample is in the monomeric fcc phase.

typically exhibits a higher g factor.²⁶ ΔH_{pp} monotonously increases from 1.8 G (100 K) to 4.0 G (280 K) respectively.

From 280 K to about 320 K, one observes dramatically transformation in EPR parameters which is explained by transition from the dimer phase to the transient monomeric fcc phase. The spin susceptibility becomes $9.8 \times 10^{-4} \text{ emu} \cdot \text{mol}^{-1}$ (300 K) and then decreases down to $5.2 \times 10^{-4} \text{ emu} \cdot \text{mol}^{-1}$ (320 K) (Fig. 5), while the linewidth increases to 12.6 G (300 K) and then decreases to 7.6 G (320 K) (Fig. 6a). The characteristic hysteresis of about 20 K around the temperature of the dimer-to-monomeric fcc phase transition is observed (Fig. 7) in agreement with

FIG 6 - The linewidth (a) and g factor (b) plotted versus temperature for the quenched sample of KC_{60} . Characteristic evolution's of these two parameters reflect phase transitions in the following sequence (see Fig. 5 and text): dimer $\rightarrow$ transient monomer fcc $\rightarrow$ polymer $\rightarrow$ intermediate ($\alpha\text{-C}_{60} + \text{K}_3\text{C}_{60}$) $\rightarrow$ monomer fcc.

other works.¹⁰ A tentative explanation for the hysteresis quoting sequentially the lattice constant of the quenched KC_{60} , the shift of transition to higher temperatures in pure C_{60} under hydrostatic pressure and the bulk modulus of C_{60} presented in Ref. 10 may be relevant here.

Above 320 K the transient monomeric fcc phase is followed by the polymeric phase, which completely replaces the predecessor at about 360 K. From 360 K to

FIG 7 - The hysteresis in the linewidth at the transition temperature between the dimer and transient monomer fcc phases of the quenched sample of KC_{60} .

380 K the polymeric phase is characterized by $g = 2.0006$ (Fig. 6b). Above 380 K to 450 K the sample is in the intermediate phase with an equilibrium state $\alpha\text{-C}_{60} + \text{K}_3\text{C}_{60}$, where the g factor of 2.0009–2.0014 is a characteristic of K_3C_{60} .³⁰

The final transition from the intermediate phase to the thermodynamically stable monomer fcc phase occurs at 450 K with another jump in χ_{EPR} from $2.2 \times 10^{-4} \text{ emu}\cdot\text{mol}^{-1}$ to $5.6 \times 10^{-4} \text{ emu}\cdot\text{mol}^{-1}$ (Fig. 5) and a drop in a g factor from 2.0006 down to 1.9997 (Fig. 6b). No transitions are observed between 450 and 500 K.

Thus from 100 K to 500 K the phase sequence for the quenched sample can be written as follows: dimer $\rightarrow$ monomer fcc $\rightarrow$ polymer $\rightarrow$ intermediate ($\alpha\text{-C}_{60} + \text{K}_3\text{C}_{60}$) $\rightarrow$ monomer fcc.

No signal of $g = 2.0025$ from C_{60}^+ radicals is observed in the room temperature spectrum (Fig. 3a). Besides, we observed this signal in low temperature spectra (not presented), but it was too weak to make considerable contribution to the temperature-independent χ_{EPR} of the slowly cooled sample. For the quenched sample, the weak Curie component of χ_{EPR} might however be partially associated with C_{60}^+ radicals.

We suspected that the high temperature treatment of C_{60} in the presence of oxygen in the sealed tube might result in $C_{60}O$ epoxides and $C_{120}O$ dimers. Adopting electrons from neighbor K atoms, such species might contribute into EPR spectra. As mentioned, we did not register signal related to $[C_{60}O]^-$. For $[C_{120}O]^{2-}$, Balch *et al.*¹⁸ have reported a single strong line with $g = 2.0016$ and $\Delta H_{pp} = 1.1$ G and doublet satellites centered at $g = 2.0030$ with spacing 13 G. For $[C_{120}O]^{4-}$, they observed a central peak with $g = 2.0025$ and four satellites centered at $g = 2.0037$.¹⁸ No such features were found in our EPR spectra either.

3.2. Differential Scanning Calorimetry

Figure 8a shows the DSC scan taken on the heating run with the rate of 10 K/min starting from the polymeric phase of the slowly cooled sample. In the 300–500 K range there are two endothermic and one exothermic peaks. The first endothermic peak at 420 K relates to the depolymerization transition when covalently bonded C_{60} molecules lose their bonds and become *freely rotating*.³¹ This leads to the formation of the intermediate state where K ions can migrate

FIG 8 - DSC thermograms recorded during heating the polymer (a) and dimer (b) phases of KC_{60} . Characteristic phases are indicated. There is a good agreement with EPR data.

resulting in instability of the KC_{60} stoichiometry. Due to migration processes, the first endothermic peak is closely followed by the exothermic peak. The second endothermic peak at 450 K is associated with the final transition into the monomer fcc phase. Hence the sequence of phase transitions for the slowly cooled sample at the heating run is: dimer $\rightarrow$ intermediate ($\alpha\text{-C}_{60} + \text{K}_3\text{C}_{60}$) $\rightarrow$ monomer fcc.

Figure 8b shows the DSC scan of the quenched sample in the 280–500 K range with three endothermic peaks. The peak at 317 K is associated with the

decomposition of the dimer phase into the transient monomeric fcc phase which is followed by the polymeric phase. The peak at 396 K relates to the polymeric-to-intermediate phase transition. At 450 K the polymeric phase transforms to the monomeric fcc phase.³¹ The obtained picture consistently agrees with EPR data.

3.3. ^{13}C Nuclear Magnetic Resonance

Figure 9 shows ^{13}C NMR spectra recorded at 295 K and 360 K for the slowly cooled sample of the polymer phase. That presented spectra are identical in shape seemed to be natural since from EPR and DSC measurements one can not expect the spectral transformation up to 400 K. Spectra demonstrate two peaks with chemical shifts of 187 ppm and 143 ppm respectively. The former value coincides with the chemical shift of K_3C_{60} ³² and the latter one relates to $\alpha\text{-C}_{60}$.³³ It is possible that some minor part of C_{60} molecules do not form covalent bonds under slow cooling so that separated areas of $\alpha\text{-C}_{60}$ and K_3C_{60} may persist in the bulk at ambient temperature. Since $g = 2.0006$ of an EPR spectrum at this temperature somewhat smaller than a typical g factor of K_3C_{60} one may conclude that such areas are indeed very small. We do not find a resonance signal which could be referred to the polymeric phase. For covalently bonded C_{60} molecules a chemical shift anisotropy (CSA) is not averaged out by a reorientation motion. This may result in such broadening that the signal can not be seen in static NMR spectra.

Figure 10 shows ^{13}C NMR spectra of the quenched sample at three characteristic temperatures. At 240 K, the essentially broad asymmetric signal is

FIG 9 - ^{13}C NMR spectra taken at (a) 295 K and (b) 360 K for the slowly cooled KC_{60} . Spectra are identical in lineshape with two peaks at 187 ppm and 143 ppm respectively. The former peak is assigned to K_3C_{60} while the latter one to K_xC_{60} ($x \ll 0.1$). We do not observe the broader signal which might be assigned to the KC_{60} polymeric phase. Perhaps the large CSA makes it too broad to be observed in static NMR spectra.

seen in vicinity of the 143 ppm line. One may relate this signal to carbons of dimerized C_{60} molecules. Since CSA in the dimer phase is likely smaller than that in the polymeric phase due to the partial motional averaging, the pertinent signal can be detected now. At 300 K the broad signal transfers to the symmetrical peak with a chemical shift of 173 ppm. This peak is assigned to the transient monomeric

FIG 10 - ^{13}C NMR spectra taken at (a) 240 K, (b) 300 K and (c) 360 K for the quenched KC_{60} . Transformation of spectral shape reflects transitions from the dimer phase (a) to the transient monomeric fcc phase (b) and then to the polymeric phase (c).

fcc phase which gradually replaces in the dimer phase.³³ With decomposition of the dimer phase one observes further transformation in the spectral shape. At 360 K the spectrum with peaks at 187 ppm and 143 ppm (Fig. 10c) is very similar to that obtained for the polymeric phase (Fig. 9b). Although our NMR probe could not be set to higher temperatures, we would expect the re-appearance of the 173 ppm line of the monomeric fcc phase in NMR spectra above 450 K. In the 240 – 360 K range NMR data satisfactorily confirm those obtained by EPR and DSC methods.

C_{60}O and C_{120}O imply ^{13}C NMR resonances at about 130-160 ppm and 75-100 ppm.^{16,17} The former resonance would belong to the fullerene skeletal carbons and the latter one would represent two/four carbons evolved in epoxide rings.^{16,17} No such lines were observed in our samples, in good agreement with EPR data.

Conclusion

Results obtained in a present study convincingly suggest that by-products of the decomposition of K_2CO_3 do not affect further polymerization and dimerization processes in KC_{60} . Only a small part of C_{60} molecules may interact with the released molecular oxygen bringing about a weak EPR signal with $g = 2.0025$. No signs of C_{60}O epoxides or C_{120}O dimers were observed in EPR and NMR spectra. Thus, alkaline carbonates can be used in preparation of C_{60} -based polymer materials where C_{60} molecules are reduced by alkaline atoms.

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