

Hindawi Publishing Corporation
Advances in Condensed Matter Physics
Volume 2008, Article ID 941372, 6 pages
doi:10.1155/2008/941372

Research Article

Superconductivity, Electron Paramagnetic Resonance, and Raman Scattering Studies of Heterofullerides with Cs and Mg

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Received 9 June 2008; Accepted 23 October 2008

Recommended by Victor Moshchalkov

In the present study, the results of investigation of physical properties of heterofullerides $A_{3-x}M_xC_{60}$ ($A=K, Rb, Cs, M=Be, Mg, Ca, Al, Fe, Tl, x = 1, 2$); as well as $RbCsTlC_{60}$, $KCsTlC_{60}$, and KMg_2C_{60} are described. All of the fullerides were synthesized by the exchange reactions of alkaline fullerides with anhydrous metal halides. Superconductivity was found in $RbCsTlC_{60}$ and $KCsTlC_{60}$.

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1. Introduction

It is well known that critical temperature of superconducting transition (T_c) of alkali-intercalated fullerides depends on the crystalline lattice parameter [1]. The value of T_c increases with the increase in some interval of the lattice parameter a . Thus one can expect that heterofullerides with Cs may possess higher T_c values because of larger a values, compared to fullerides with K and Rb. Fulleride Cs_3C_{60} , synthesized by standard gaseous method, has primitive cubic lattice and is not a superconductor. Under high pressure, Cs_3C_{60} is a superconductor with $T_c = 40$ K in FCC lattice as well as K_3C_{60} and Rb_3C_{60} . The efforts to synthesize fullerides with composition from Cs_2C_{60} to Cs_6C_{60} in a solvent (toluol) give amorphous or polymerized non-superconducting substances [2]. It is worth to note that for KCs_2C_{60} and $RbCs_2C_{60}$ fullerides, both methods produce superconductors with the same T_c .

We showed that exchange reaction of homofullerides of K and Rb with anhydrous group 8–10 metal halides rear earth metal halides in tetrahydrofuran substitute a part of alkali metal to Ln or Fe with surviving of superconductivity [3, 4]. The open question is as follows: are these substances superconductors themselves or they are partly defected fullerides K_3C_{60} and Rb_3C_{60} ? To check the effectiveness of exchange reaction, we tried to synthesize by the same

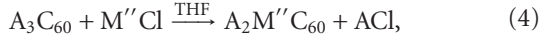
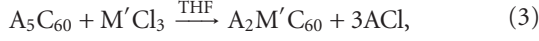
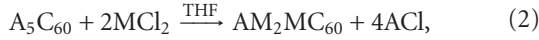
method the heterofullerides with Cs. The Cs fullerides under normal conditions are non-superconductors, that is why the observation of superconductivity when some atoms of Cs replaced by metal of will be an evidence of superconducting properties of heterofullerides with other not alkali metals.

2. Experimental

Toluene and tetrahydrofuran (THF) were cleared and absolutized by standard techniques. Anhydrous metal chlorides were also obtained by standard techniques; chlorides of beryllium, aluminum, and iron were synthesized by chlorination of metal by dry chlorine; chlorides of magnesium, calcium, barium, and strontium were received by thermal drying of hydrated salts with ammonium chloride in vacuum; thallium chloride was commercially available. Potassium, rubidium, and caesium fullerides were synthesized by reaction of fullerite with the stehiometric quantity of metal in the environment of toluene at 120–130°C by a method described in [5].

Synthesis of the initial of alkali metal fullerides, partial removal of toluene, blending of fulleride suspension with suspension of heterometal halogenide in THF, drying of products of reaction, and their packaging in ampoules for definition of temperature of superconducting transition were carried out in vacuum in the full glass facilities equipment.

In more detail, the technique is described in [4, 5]. The exchange reactions are writing as



where A—K, Rb, Cs; M—Be, Mg, Ca; M'—Al, Fe; M''—Tl.

The measurements of RFA were carried out with Guinier G670 HUBER. The sample of fullerene was located in a thin-walled glass capillary which was brazed in vacuum. C^{13} NMR spectra are measured by Bruker AC-200 under the one-pulse program with duration of excitation impulse 4 microseconds. Intervals between impulses was 2 seconds. For measurements of Raman spectra Perkin-Elmer Raman spectrometer with He-Ne, the laser with wavelengths of 632.7 nanometers was used. Measurements of EPR spectra were carried out on EPR spectrometer Bruker (model Elexsys 500) in the X-range with flow cryostat in temperature interval of 105–300 K. The values of g-factors were calculated based on reference line of Mn^{2+} ions in MgO ($g = 1.9812$).

Temperatures of superconducting transitions of fullerides were defined by standard low-frequency induction method by measuring the temperature dependence of a magnetic susceptibility in temperature interval $4.2 < T < 300$ K.

3. Results and Discussion

3.1. Superconductivity

Fullerides $RbCsTlC_{60}$ and Rb_2TlC_{60} have superconducting transition temperature T_c higher than others. For $KCsTlC_{60}$, the value of $T_c = 21.7$ K is the highest for fullerides with K. Fullerides with composition $Cs_{3-x}M_xC_{60}$ (M—metal, $x = 1, 2$) are non-superconductors. We found that T_c of fullerides with composition K_2MC_{60} is lower than that of K_3C_{60} (excluding $KCsTlC_{60}$, with $T_c = 21.7$ K). Moreover, there is a correlation between lattice constant of these fullerides and their T_c , namely, lattice constant of K_2MC_{60} fullerides (excluding $KCsTlC_{60}$) is smaller than lattice constant of K_3C_{60} due to smaller radii of ion substituting ion K^+ .

Superconductivity of triple heterofullerides $RbCsTlC_{60}$ at $T_c = 26.4$ K, $KCsTlC_{60}$ at $T_c = 21.7$ K, and a heterofulleride Rb_2TlC_{60} at $T_c = 27.2$ K was discovered by investigation of temperature dependence of magnetic susceptibility. Temperature dependencies of magnetic susceptibility of these compounds are plotted in Figure 1. It should be mentioned that $RbCsTlC_{60}$ and Rb_2TlC_{60} transfer to superconducting state at temperatures higher than T_c values of our previously investigated heterofullerides, synthesized by the same method. The $T_c = 24.5$ K of Rb_2BeC_{60} was maximal, that was achieved previously [4, 6]. The fulleride $KCsTlC_{60}$ possesses the highest $T_c = 21.7$ K among all synthesized in the present study of heterofullerides with potassium. This confirms the suggestion that the increase of the T_c value

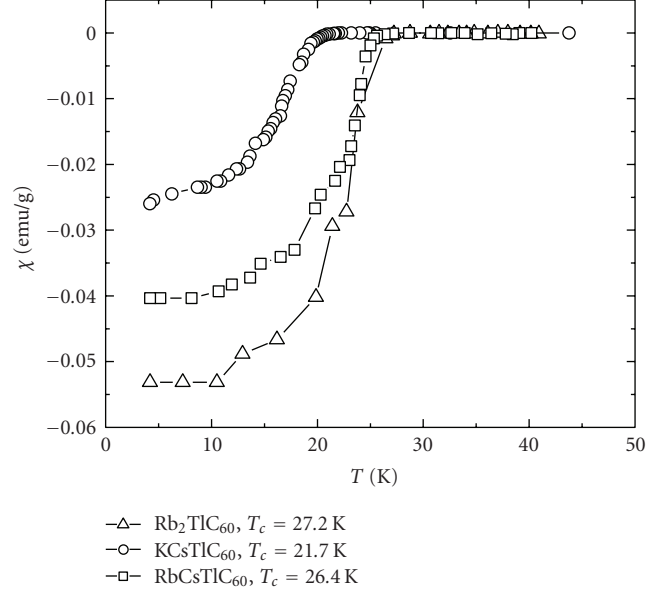


FIGURE 1: Temperature dependencies of magnetic susceptibility of $RbCsTlC_{60}$, $KCsTlC_{60}$, and Rb_2TlC_{60} . Superconductivity was found in new fullerides with Cs.

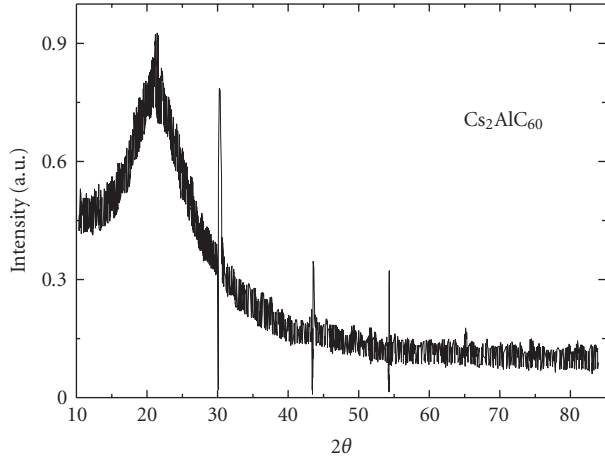
TABLE 1: Composition, superconducting transition temperature (T_c), crystal lattice parameter (a), and ionic radius of heterometal (r^+) for some investigated fullerides.

Composition	T_c (K)	a (Å)	r^+ (Å)
K_3C_{60}	18.5	14.3110(5)	1.33
Rb_2TlC_{60}	27.2	14.448(6)	(+3e) 0.95 (+1e) 1.47
$KCsTlC_{60}$	21.7	14.424(14)	(+3e) 0.95 (+1e) 1.47
$RbCsTlC_{60}$	26.4	14.673(17)	(+3e) 0.95 (+1e) 1.47

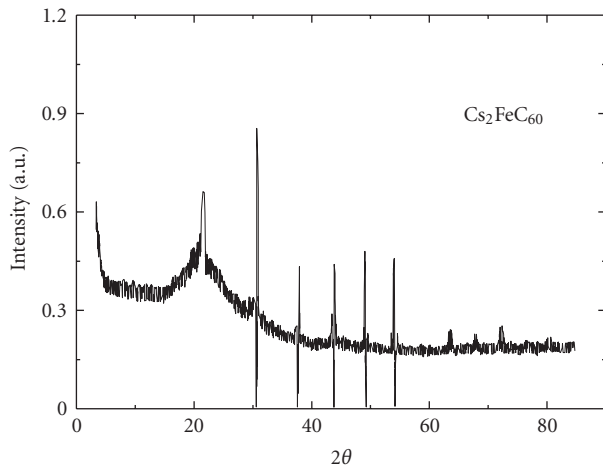
is due to the increase of the lattice constant caused by substitution of K and Rb by Cs. $KCsTlC_{60}$ has maximal value of a ($a = 1.442$ nm compared to K_3C_{60} $a = 1.431$ nm) among all superconducting heterofullerides with potassium. The same is for $RbCsTlC_{60}$ ($a = 1.467$ nm, Rb_2BeC_{60} $a = 1.445$ nm). Such appreciable increase of the parameter a of FCC lattice is quite naturally and also is one more proof of intercalation of atoms of bigger sizes in fullerene structure. There were no superconducting transitions in heterofullerides with more than one Cs atom per fullerene C_{60} . In Table 1, parameters of two superconducting fullerides with Cs are shown together with K_3C_{60} and Rb_2TlC_{60} for comparison.

3.2. X-ray Data

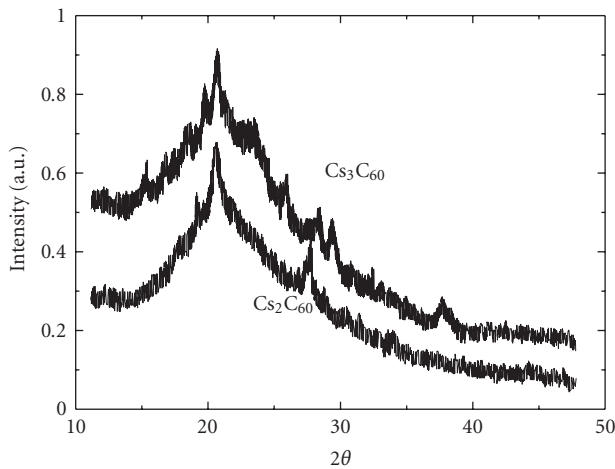
According to RFA, data majority of heterofullerides with Cs are amorphous. All attempts to synthesize caesium heterofullerides by interaction of homofullerides Cs_nC_{60}



(a)



(b)



(c)

FIGURE 2: Diffractogram of $\text{Cs}_2\text{AlC}_{60}$, $\text{Cs}_2\text{FeC}_{60}$, and Cs_2C_{60} , Cs_3C_{60} . Vertical lines show peaks of CsCl . There is no reflection from fulleride crystal lattice.

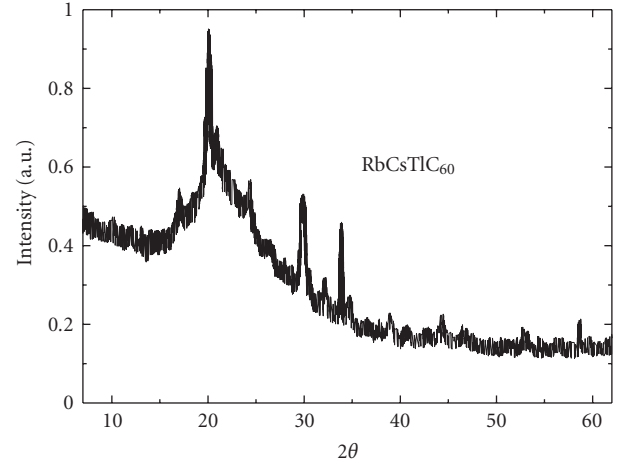


FIGURE 3: Diffractogram of fulleride RbCsTlC_{60} synthesized by (4) mixed with the product of reaction CsCl .

with chlorides of beryllium, magnesium, calcium, barium, aluminum, and iron on (1) and (3) lead to non-superconducting X-ray amorphous samples (Figure 2). One can see only wide peak (halo) at $2\theta \approx 20.2^\circ$ and peaks identified as crystalline CsCl in X-ray spectrum. As in C^{13} NMR spectra of these samples, there is no resonance at 170–200 ppm, which is common for all homo- and heterofullerides with FCC lattice with freely rotating anion C_{60}^{-n} . We assume that caesium fullerides are not simply amorphous, but polymeric substances.

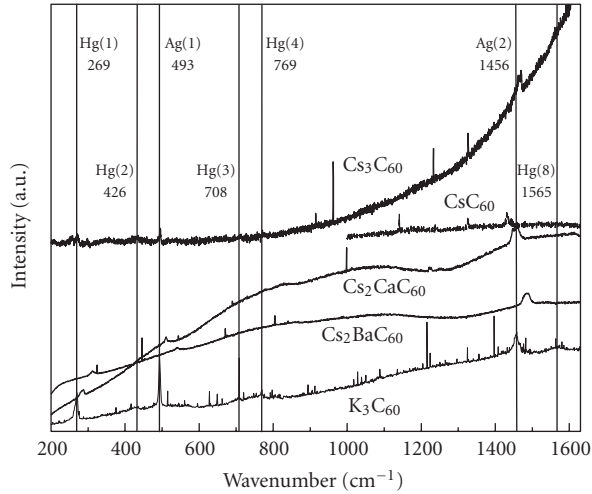
The results of interaction of Cs_3C_{60} with TlCl , according to (4), do not give any new information. But in reaction of thallium chloride with alkali metal heterofullerides, according to (4), obtained heterofullerides are crystalline substances (Figure 3) and superconductors.

3.3. Raman Scattering

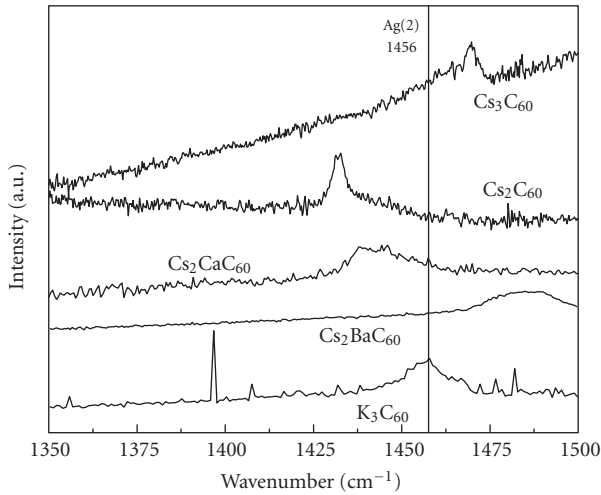
The results of measurement and investigation of Raman scattering of fullerides Cs_2C_{60} , Cs_3C_{60} , $\text{Cs}_2\text{MC}_{60}$ ($M=\text{Ca}, \text{Ba}$) showed that these fullerides are most likely not crystalline. This is testified by the absence of nearly all characteristic fullerene C_{60} phonon modes (Figure 4). The lines in Raman spectra are strongly shifted and extended compared to the lines of pure fullerite. Thus one cannot definitely identify presented lines and estimate the charge state of C_{60} molecule in these compounds.

The absence of the majority of oscillatory modes observed in K_3C_{60} spectrum specifies polymerization (more rigid fixing of molecules C_{60}).

On the basis of X-ray and Raman spectra, one can conclude that fullerides and heterofullerides of caesium are polymers. This fact can explain the absence of superconductivity in these compounds because polymerization suppresses the phonon modes of C_{60} molecules that mediate electron-electron attraction [7]. Besides, polymerization may cause transition to the dielectric state.



(a)



(b)

FIGURE 4: Raman scattering spectra of fullerides Cs_2C_{60} , Cs_3C_{60} , and $\text{Cs}_2\text{MC}_{60}$ ($M=\text{Ca}, \text{Ba}$) obtained at (a) room temperature and (b) Raman spectra in the range near line Ag(2) of K_3C_{60} for the same fullerides.

3.4. Electron Paramagnetic Resonance

In EPR spectrum of $\text{CsMg}_2\text{C}_{60}$, there are two lines, the second one has higher g -factor and is much wider than the main line. Parameters of this line are shown in Table 2. Intensity of this line decreases as temperature decreases and it is not visible for $T < 120$ K. The most probably explanation of the drastically decrease of the intensity is due to transition of paramagnetic centers to the different spin states. The nature of these centers at the moment is unknown.

The analysis of electron paramagnetic resonance (EPR) spectra and their temperature dependence revealed the presence of at least two different types of paramagnetic centers, that is, two lines of different widths, in superconducting fullerides A_2MC_{60} ($A=\text{K}, \text{Rb}, M=\text{Be}, \text{Mg}$)—Figure 5.

Temperature dependence of paramagnetic susceptibility (double-integrated EPR signal) of narrow line is described

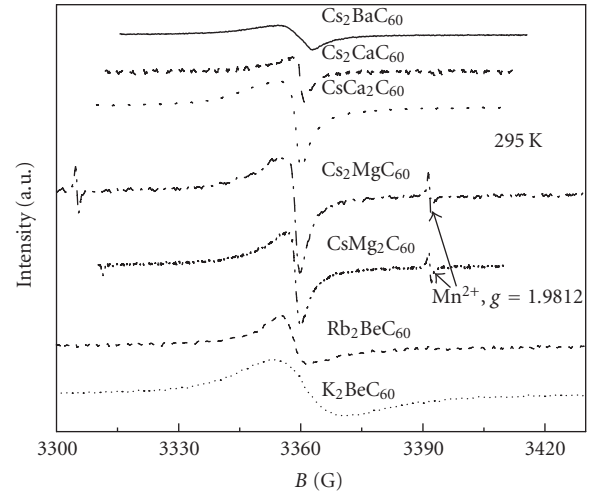


FIGURE 5: Asymmetric of EPR spectra heterofullerides with Cs pointed out to asymmetric environment of molecule C_{60} due to possible polymerization.

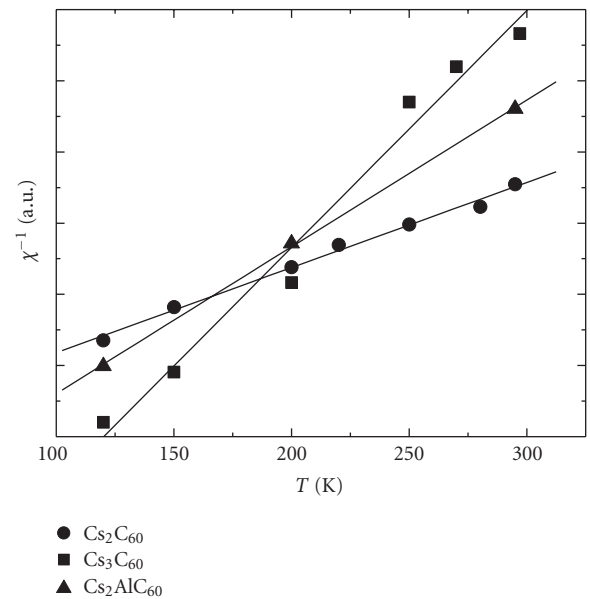


FIGURE 6: Temperature dependence of paramagnetic susceptibility χ (double-integrated EPR signal) non-superconducting fullerides with Cs. Curie-Weiss law (fitting by solid lines) is a consequence of the absence of conduction electrons (no contribution to the paramagnetic susceptibility).

by Curie-Weiss law Figure 6. Therefore, the appropriate paramagnetic centers obey Boltzman statistics and probably are due to electron-charged defects like $\text{C}_{60}-\text{O}$ or $\text{C}_{60}-\text{O}-\text{C}_{60}$ [8, 9]. Temperature dependence of parameters of broad line (second type of centers) is weak. This points out to the Fermi statistics of the centers of the second type, presumably they are conduction electrons [10, 11].

At the same time, EPR spectra of non-superconducting fullerides with the composition Cs_xC_{60} ($x = 2, 3$), $\text{Cs}_2\text{AlC}_{60}$ can be described by anisotropic signal of only one type of

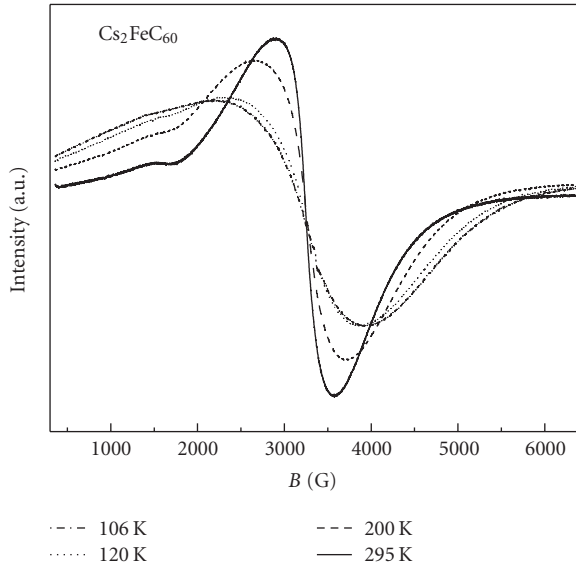


FIGURE 7: EPR spectra at different temperatures of $\text{Cs}_2\text{FeC}_{60}$.

TABLE 2: Average line width ΔHpp and g -factor of EPR for non-superconducting fullerides of Cs and Mg.

Composition	ΔHpp and g -factor	T (K)		
		297	200	120
$\text{Cs}_2\text{MgC}_{60}$	g		2.0010 ± 0.0003	
	ΔHpp (Oe)	4.8	5.4	7.3
$\text{CsMg}_2\text{C}_{60}$	g		2.0010 ± 0.0003	
	ΔHpp (Oe)	3.3	4.4	7.2
$\text{CsMg}_2\text{C}_{60}$ (wide line)	g	2.2335	2.2785	—
	ΔHpp (Oe)	248	221	—
$\text{K}_2\text{MgC}_{60}$	g		2.0010 ± 0.0003	
	ΔHpp (Oe)	3.7	2.7	2.1
$\text{KMg}_2\text{C}_{60}$	g		2.0009 ± 0.0003	
	ΔHpp (Oe)	5	2.4	1.8

paramagnetic signals with Boltzmann statistics, that is, defects with odd electron charge. This follows from temperature dependence of lineshape and paramagnetic susceptibility, calculated by double integration of EPR spectra. In the investigated temperature range (105 K–300 K), paramagnetic susceptibility can be well fitted by Curie-Weiss law. The extraction of the signal from conducting electrons with temperature-independent paramagnetic susceptibility for EPR spectra of these fullerides is not possible, indicating that the density of electrons is low. This fact is confirmed by the absence of superconducting transition in these fullerides.

In Figure 7, we plotted EPR spectra for $\text{Cs}_2\text{FeC}_{60}$ fulleride. The width of the line increases while the amplitude decreases when temperature decreases, notification of ferromagnetic resonance. Some parameters of EPR signals for non-superconducting fullerides are listed in Table 2.

4. Conclusions

Exchange reactions of caesium fullerides with anhydrous metal chlorides lead to polymeric and non-superconducting phases. The exception is ternary fullerides with supposed composition of RbCsTiC_{60} with $T_c = 26.4$ K and KCsTiC_{60} with $T_c = 21.7$ K. As it is known for alkali metal fullerides, T_c depends linearly on the lattice parameter a and the same linear law was found for synthesized superconducting heterofullerides.

The EPR spectra of non-superconducting fullerides with the composition Cs_nC_{60} ($n = 2, 3$), $\text{Cs}_2\text{AlC}_{60}$ can be described by anisotropic signal, that originates from one type of paramagnetic centers with Boltzmann statistics. Most likely, these centers are odd-charged defects $\text{C}_{60}-\text{O}$ or $\text{C}_{60}-\text{O}-\text{C}_{60}$. The results of measurement and investigation of Raman scattering of fullerides Cs_2C_{60} , Cs_3C_{60} , $\text{Cs}_2\text{MC}_{60}$ ($M=\text{Ca}, \text{Ba}$) showed that these fullerides are polymers. This fact simultaneously with absence of conduction electrons can explain the non-superconducting character of these compounds because polymerization suppresses the phonon modes of C_{60} molecules that mediate electron-electron attraction.

Acknowledgment

The work was supported by RFBR, Grant no. 08-03-00237-a. The measurements of EPR and Raman spectra were carried out on the equipment of the Center of Users' Facilities of Moscow State University.

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