

# High-resolution thermal expansion of superconducting fullerenes $A_3C_{60}$ ( $A = K, Rb$ )

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The thermal expansion of air-sensitive  $A_3C_{60}$  compounds ( $A = K, Rb$ ) was investigated using a high-resolution capacitance dilatometer operating in an inert atmosphere. The discontinuity in the linear thermal expansivity at the superconducting transition,  $\Delta\alpha$ , of each compound is presented, from which we determine the corresponding discontinuity in the specific heat  $\Delta c_p/T_c$ , via the Ehrenfest relation ( $75 \pm 14$  mJ/mol K<sup>2</sup> for  $Rb_3C_{60}$  and  $64 \pm 14$  mJ/mol K<sup>2</sup> for  $K_3C_{60}$ ). On the basis of the calculated  $\Delta c_p/T_c$  values, the density of states  $N(E_F)$  and the electron-phonon coupling constant  $\lambda$  are derived using the McMillan strong-coupling formalism and recent theoretical results. We find  $N(E_F) = 6.6 \pm 1.1$  states/eV spin  $C_{60}$  and  $7.4 \pm 1.0$  states/eV spin  $C_{60}$  for  $K_3C_{60}$  and  $Rb_3C_{60}$ , respectively. The associated  $\lambda$  is estimated to be  $\sim 0.5$  for both  $K_3C_{60}$  and  $Rb_3C_{60}$ . The ratio  $N(E_F)_{Rb_3C_{60}}/N(E_F)_{K_3C_{60}}$  is consistent with a superconducting mechanism involving high-frequency intramolecular phonons. [S0163-1829(96)50534-5]

Extensive experimental and theoretical investigations of superconductivity in alkali-metal-intercalated fullerenes with transition temperatures  $T_c$  up to 33 K (Ref. 1) support strongly a superconducting mechanism on the basis of a phonon-mediated electron-electron interaction.<sup>2</sup> The exceptionally high  $T_c$  values (for electron-phonon coupling) have been rationalized on the basis of two unusual properties of doped  $C_{60}$ . First, because of the strong covalent bonding within a  $C_{60}$  molecule, there are high-energetic intramolecular vibrations giving a high associated frequency  $\omega_D$  for these phonons.<sup>3</sup> Second, the large intermolecular distance of adjacent  $C_{60}^{3-}$ -ions results in narrow electronic conduction bands and a correspondingly high density of states  $N(E_F)$  at the Fermi level.<sup>4</sup> These large  $N(E_F)$  and  $\omega_D$  can account quantitatively for the high  $T_c$  values within a strong-coupling modified BCS theory<sup>5</sup> with a McMillan parameter  $\lambda$  of about 0.5–1.0 (Ref. 6). Whereas many experimental results, e.g., pressure studies,<sup>7</sup> are consistent with the above scenario, there is still currently a wide variation in both experimentally and theoretically derived values for  $N(E_F)$  and  $\lambda$ ,<sup>8</sup> and more experiments on well-characterized samples are needed. An investigation of the specific heat jump at the superconducting transition can make a valuable contribution in determining these quantities. Surprisingly, up to now only one investigation of the specific heat of fullerenes has been published, performed for  $K_3C_{60}$  by Ramirez *et al.*<sup>9</sup> This is most likely caused by the extreme reactivity of the fullerenes to air, which makes an encapsulation of the sample mandatory thereby complicating significantly the experiment.

In this paper we present high-resolution thermal expansion data of both  $K_3C_{60}$  and  $Rb_3C_{60}$ , from which we determine the specific heat anomalies at  $T_c$  using the Ehrenfest relationship

$$\frac{dT_c}{dp} = 3V_{\text{mol}}T_c \frac{\Delta\alpha}{\Delta c_p}. \quad (1)$$

This thermodynamic relation correlates the jump in the thermal expansivity at the superconducting transition,  $\Delta\alpha(T_c)$ , with the jump in the specific heat at  $T_c$ ,  $\Delta c_p(T_c)$ , and the

pressure dependence of  $T_c$ ,  $dT_c/dp$ , the latter of which has been measured accurately.<sup>7</sup> We show that the derived  $\Delta c_p/T_c$  value for  $K_3C_{60}$  is in excellent agreement with the direct specific heat measurement,<sup>9</sup> and that the ratio of the specific heat anomalies of  $K_3C_{60}$  and  $Rb_3C_{60}$  is consistent with a coupling mechanism involving intramolecular phonons. On the other hand, the  $N(E_F)$  values derived from our data lie at the bottom of the range of theoretically derived  $N(E_F)$ 's.<sup>6</sup>

The thermal expansion of the fullerenes was investigated using a high-resolution parallel-plate capacitance dilatometer with a resolution of  $\Delta L \sim 0.05$  Å. Because of the fullerenes extreme sensitivity to air, the preparation, the characterization as well as the measurements of the thermal expansion have to be performed in an inert gas atmosphere. For this purpose, a dilatometer cell was designed, in which the samples can be mounted directly in an argon atmosphere glove box ( $O_2 < 1$  ppm;  $H_2O < 0.1$  ppm). After transfer of the dilatometer cell to the cryostat, the argon atmosphere in the cell is exchanged by a helium atmosphere to ensure thermal contact during the dilatation measurements.

To prepare  $K_3C_{60}$  and  $Rb_3C_{60}$  powder samples, stoichiometric quantities of (two times) sublimed  $C_{60}$  powder and alkali metal were sealed in quartz ampoules, reacted at 350 °C for several days, pelletized (3–5 mm height, 3 mm diameter) and again tempered at 350 °C for several days. Afterwards the samples were characterized by both powder x-ray diffraction ( $Cu-K_\alpha$ ) and by magnetization measurements (SQUID). A second characterization was performed for several samples after dilatometry to test the working of the inert gas handling system of the new device.

Figure 1(a) shows the powder diffraction data for a freshly prepared  $K_3C_{60}$  sample. Also plotted is a Rietveld refinement of the data, which gives no indication of any impurity phase at the 5–10 % level. However, as will be shown later, the thermal expansion measurements demonstrate clearly that this sample is two-phased, with about 7%  $\alpha$ - $C_{60}$  (see below and Fig. 3). In Fig. 1(b) the powder diffraction pattern of a  $Rb_3C_{60}$  sample is shown, which was made after dilatometer measurements in order to verify the

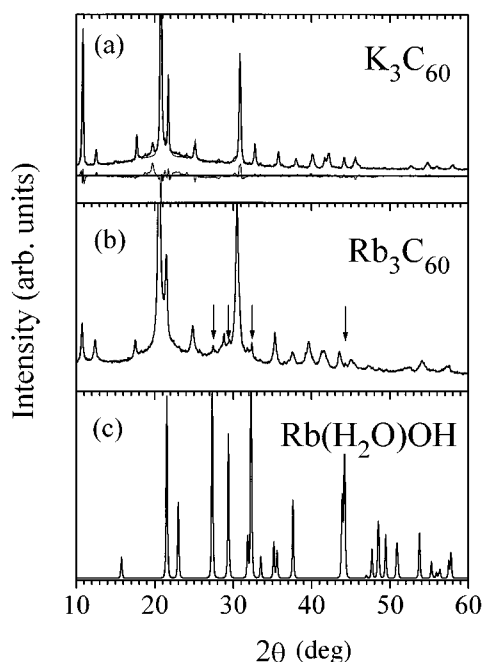


FIG. 1. (a) Powder diffraction pattern (Cu- $K_\alpha$  radiation) of  $K_3C_{60}$ , together with a Rietveld refinement fit of the  $K_3C_{60}$  structure taken from Ref. 28. (b) Powder diffraction pattern (Cu- $K_\alpha$  radiation) of  $Rb_3C_{60}$ . The arrows point to peaks of a small amount of  $Rb(H_2O)OH$  (see text for details). (c) Calculated powder diffraction pattern for  $Rb(H_2O)OH$  based on a structural proposal by Jacobs *et al.*<sup>10</sup>

stability of these extremely air-sensitive samples during the experimental investigation. This diffraction pattern shows little difference from the pattern of a freshly prepared sample (not shown), except for the appearance of several small additional peaks (marked by arrows). These additional peaks are related to the hydroxidemonohydrate compound  $Rb(H_2O)OH$ , indicating a degradation of the sample most likely on a 5% level caused by a chemical reaction of rubidium with residual water vapor in the “inert” gas atmosphere (argon and helium). Figure 1(c) shows a calculated

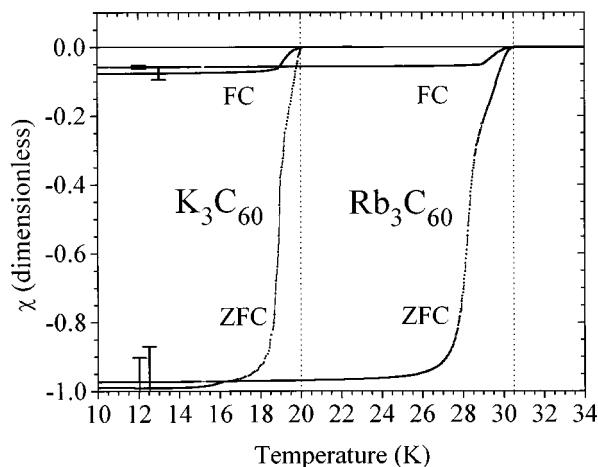


FIG. 2. Magnetic susceptibility  $\chi$  of  $K_3C_{60}$  and  $Rb_3C_{60}$  derived by field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements performed with a self-constructed SQUID magnetometer.

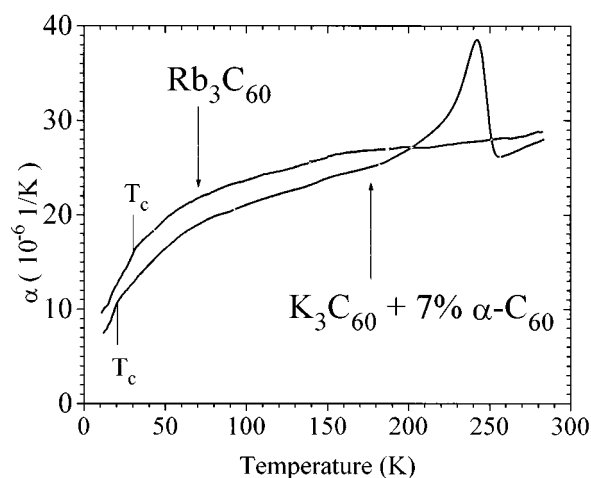


FIG. 3. Linear thermal expansivity of  $K_3C_{60}$  and  $Rb_3C_{60}$ . The anomaly in the thermal expansivity of the  $K_3C_{60}$  sample near  $T^* \sim 242$  K is related to the orientational order-disorder transition of a small amount of  $\alpha-C_{60}$  (see text for details).

diffraction pattern of  $Rb(H_2O)OH$  based on a structure proposal by Jacobs *et al.*<sup>10</sup> This reaction is different from the reaction of alkali-metal intercalated fullerenes with pure oxygen, identified by Snyder *et al.*,<sup>11</sup> and was studied in more detail in a  $Rb_6C_{60}$  sample.<sup>12</sup>

The magnetization of the  $K_3C_{60}$  and  $Rb_3C_{60}$  samples was measured with a self-constructed SQUID magnetometer, which is shielded magnetically by  $\mu$  metal allowing low-field measurements (the residual earth magnetic field strength is less than  $2 \times 10^{-3}$  Oe). The magnetometer was calibrated using Pb samples of the same geometry as the fulleride samples. The measurements shown in Fig. 2 are performed at a magnetic field strength of  $H=1.3$  Oe ( $Rb_3C_{60}$ ) and  $H=0.6$  Oe ( $K_3C_{60}$ ). Fairly sharp superconducting transitions with onset temperatures of 20 and 30.5 K are observed for  $K_3C_{60}$  and  $Rb_3C_{60}$ , respectively. The low-temperature susceptibility observed in the zero-field-cooled (ZFC) mode yields complete shielding for both samples within the error of the measurements ( $K_3C_{60}$ :  $\chi_{ZFC} \sim -0.99$ ;  $Rb_3C_{60}$ :  $\chi_{ZFC} \sim -0.97$ ). In contrast the Meissner effect, i.e., field-cooled (FC) mode, is smaller than 10% [ $K_3C_{60}$ :  $\chi_{FC} \sim -0.08(\pm 0.02)$ ;  $Rb_3C_{60}$ :  $\chi_{FC} \sim -0.07(\pm 0.01)$ ]. Furthermore, a kink in the susceptibility is observed below  $T_c$  for both the ZFC and the FC data, which is attributed to intergranular shielding.<sup>13</sup> The above behavior is typical for a polycrystalline type-II superconductor<sup>14</sup> and indicates that the majority phase is the  $A_3C_{60}$  superconducting phase in agreement with our x-ray results. Low Meissner fractions are often observed in type-II superconductors with flux pinning<sup>15</sup> and do not imply necessarily a low superconducting fraction. On the other hand, these types of measurements do not allow an unambiguous determination of the superconducting volume fraction.

It is important to note that the fraction of the superconducting phase  $A_3C_{60}$  is correlated directly with the jump height in the thermal expansivity at the superconducting transition temperature, and thus, it is essential to analyze accurately the phase composition of the samples. Within the resolution of the just discussed characterization techniques,

the  $A_3C_{60}$  phase is the majority phase with a fraction of more than 90%. For the following interpretation of the thermal expansion measurements the samples are assumed to be single phase  $A_3C_{60}$  samples and, therefore, the estimated values for  $\Delta\alpha(T_c)$  and  $\Delta c_p(T_c)$  are lower limits.

The linear thermal expansivity  $\alpha(T)$  of the  $K_3C_{60}$  and  $Rb_3C_{60}$  samples is shown in Fig. 3 in the temperature range 10–290 K. A pronounced anomaly is seen in the thermal expansivity of the  $K_3C_{60}$  sample at  $T^* \sim 242$  K, which we attribute to the orientational order-disorder transition of a small amount of  $\alpha-C_{60}$  phase in this sample. The existence of  $\alpha-C_{60}$  is consistent with the phase diagram<sup>16</sup> and suggests that the overall K stoichiometry of the sample is slightly below 3. Using the relative change in length caused by the order-disorder transition in pristine  $C_{60}$  (Ref. 17), an impurity of about 7%  $\alpha-C_{60}$  is estimated for the present  $K_3C_{60}$  sample. It is interesting to note that the ordering transition in  $\alpha-C_{60}$  is depressed by about 19 K from that in pristine  $C_{60}$  (Refs. 17,18). This is most likely caused by a kind of “negative chemical pressure” because of intercalation with potassium atoms, which increases the intermolecular separation. This interpretation is in accord with experiments on the hydrostatic pressure dependence of  $T^*$  in pristine  $C_{60}$ , where the orientational order-disorder transition is shifted to higher temperatures while the pressure is raised.<sup>19</sup> We never observed any anomalies in the Rb-doped samples near 250 K. This is consistent with the different phase diagram of Rb-doped  $C_{60}$ , in which the  $RbC_{60}$  phase, unlike the metastable  $KC_{60}$ , does not phase separate into the respective  $\alpha-C_{60}$  and  $A_3C_{60}$  phases.<sup>16</sup> Except for the  $\alpha-C_{60}$  induced anomaly, the shapes of the thermal expansivities of  $K_3C_{60}$  and  $Rb_3C_{60}$  are quite similar over the complete temperature range; the values for  $Rb_3C_{60}$  are about 10% larger than the ones for  $K_3C_{60}$ . The thermal expansivities at room temperature,  $\sim 28 \times 10^{-6}$  1/K ( $K_3C_{60}$ ) and  $\sim 29 \times 10^{-6}$  1/K ( $Rb_3C_{60}$ ), are quite large and the value for  $Rb_3C_{60}$  agrees well with the one obtained by Zhou *et al.*<sup>20</sup> using x-ray diffraction between room temperature and 400 °C ( $30.5 \times 10^{-6}$  1/K). It should be noted that the expansivities of the  $A_3C_{60}$  phases are surprisingly large. In comparison, the expansivity of pristine  $C_{60}$  at room temperature is only about one half as large<sup>17</sup> ( $\alpha_{C_{60}}/\alpha_{Rb_3C_{60}} \sim 16 \times 10^{-6} \text{ K}^{-1}/30 \times 10^{-6} \text{ K}^{-1} = 0.53$ ) as that of the  $A_3C_{60}$  compounds, even so the intermolecular potential is softer for pristine  $C_{60}$  as implied by the compressibilities  $\kappa$  ( $\kappa_{C_{60}}/\kappa_{Rb_3C_{60}} \sim 20.5 \text{ GPa}/13.4 \text{ GPa} = 1.53$ ) (Refs. 19,21). This may be an indication for extremely anharmonic interactions between the alkali metal and the  $C_{60}$  molecules.

An interesting consequence of the large thermal expansion (the change in volume  $\Delta V/V$  is about 2% in the range 10–290 K) is that the density of states at the Fermi level  $N(E_F)$ , which is correlated with the lattice parameter  $a$  (Refs. 22,23), will have a significant temperature dependence. Using the  $N(E_F)$  vs a dependence from Tanigaki *et al.*<sup>22</sup> (for intramolecular phonons), we calculate a decrease of  $N(E_F)$  caused by thermal contraction from room temperature to  $T_c$  of about 6% and 8% for  $Rb_3C_{60}$  and  $K_3C_{60}$ , respectively. This correction also is considered in electronic band structure calculations, which predicts a 15% reduction of the density of states  $N(E_F)$  for  $K_3C_{60}$  in the temperature range

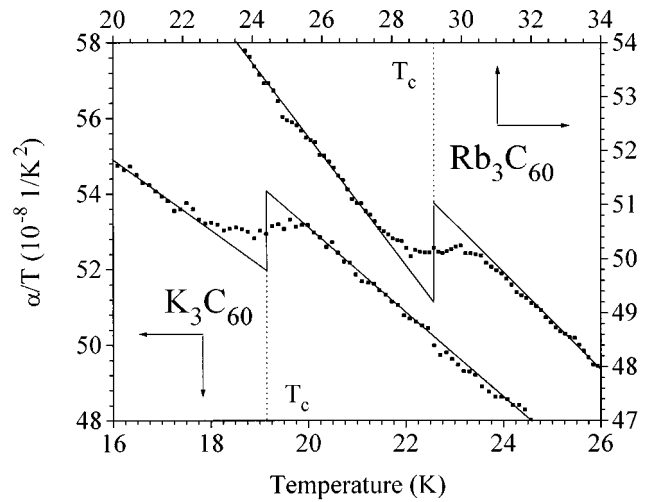


FIG. 4. Thermal expansivity  $\alpha/T$  of  $K_3C_{60}$  and  $Rb_3C_{60}$  in the vicinity of the superconducting transition. The solid lines show a fit to an idealized discontinuity used to analyze the jump height. Discontinuities in the thermal expansivity, as expected for a second-order phase transition to superconductivity, are seen for  $Rb_3C_{60}$  at  $T_c \sim 29$  K and for  $K_3C_{60}$  at  $T_c \sim 19$  K.

10–300 K (Ref. 23) (regarding a contraction  $\Delta a/a \sim 6-7 \times 10^{-3}$  of the lattice parameter).

In Fig. 4 the thermal expansivity of  $K_3C_{60}$  and  $Rb_3C_{60}$  is shown in the vicinity of  $T_c$  in a  $\alpha/T$  vs  $T$  plot. Clear anomalies in  $\alpha$  are seen at the respective critical temperatures of both  $K_3C_{60}$  and  $Rb_3C_{60}$ . The solid lines represent the idealized discontinuities expected for a second-order phase transition and were used to determine the  $\Delta\alpha$  values  $\Delta\alpha(T_c) = \alpha_S - \alpha_N = -(5.4 \pm 0.9) \times 10^{-7}$  1/K for  $Rb_3C_{60}$  and  $\Delta\alpha(T_c) = -(3.8 \pm 0.8) \times 10^{-7}$  1/K for  $K_3C_{60}$ . Incorporating these  $\Delta\alpha(T_c)$  and the  $dT_c/dp$  values from Sparn *et al.*<sup>7</sup> the Ehrenfest relation yields  $\Delta c_p/T_c$  values of  $75 \pm 14$  mJ/mol K<sup>2</sup> and  $64 \pm 14$  mJ/mol K<sup>2</sup> for  $Rb_3C_{60}$  and  $K_3C_{60}$ , respectively. For  $K_3C_{60}$  this  $\Delta c_p/T_c$  value agrees very well with the one obtained directly from specific heat measurements<sup>9</sup> ( $\Delta c_p/T_c = 68 \pm 13$  mJ/mol K<sup>2</sup>), verifying the present approach.

In the following, we discuss our results within the strong-coupling modified BCS theory. Our discussion differs from that of Ramirez *et al.*,<sup>9</sup> who for  $K_3C_{60}$  obtained very similar experimental results, in that we make use of a recent theoretical result which relates directly the McMillan parameter  $\lambda$  with  $N(E_F)$  (Ref. 6) and which, thus, allows a direct consistency check between experiment and theory.  $\Delta c_p/T_c$  is related directly to microscopic parameters within the BCS theory of superconductivity.

$$\frac{\Delta c_p}{T_c} \approx 1.43 \gamma = 1.43 \frac{2}{3} \pi^2 k_B^2 N(E_F). \quad (2)$$

For a strong electron-phonon interaction, Eq. (2) is modified by the McMillan-parameter  $\lambda$  (Ref. 24)

$$\frac{\Delta c_p}{T_c} \approx \frac{2}{3} \pi^2 k_B^2 N(E_F) (1 + \lambda) [1.43 + O(\lambda^2)]. \quad (3)$$

Thus,  $\Delta c_p/T_c$  depends on both the density of states  $N(E_F)$  and the McMillan parameter  $\lambda$ . Recent detailed *ab initio* calculations of the electron-phonon coupling strength (only intramolecular phonons are considered) give  $\lambda = 0.068N(E_F)$ .<sup>6</sup> This explicit relation allows us to extract both  $N(E_F)$  and  $\lambda$  from our derived  $\Delta c_p/T_c$  values using Eq. (3). Within this framework  $N(E_F)$  is equal to  $7.4 \pm 1.0$  states/eV spin  $C_{60}$  and  $6.6 \pm 1.1$  states/eV spin  $C_{60}$ , for  $Rb_3C_{60}$  and  $K_3C_{60}$ , respectively. Associated  $\lambda$  values are  $0.50 \pm 0.07$  ( $Rb_3C_{60}$ ) and  $0.45 \pm 0.07$  ( $K_3C_{60}$ ).

As has been discussed by Antropov *et al.*,<sup>6</sup> there exists a large uncertainty in theoretically derived  $N(E_F)$  values, where  $N(E_F)$  was estimated to fall in the ranges 6.7–8.6 states/eV spin  $C_{60}$  and 7.5–10 states/eV spin  $C_{60}$  for  $K_3C_{60}$  and  $Rb_3C_{60}$ , respectively. Our currently derived values lie at the bottom end of this range and are about a factor of 1.5–3 smaller than  $N(E_F)$  values estimated from other experiments (see Ref. 2, p. 62). Recent modeling of the photoemission spectra of  $C_{60}$  (Ref. 25) indicate that the electron phonon coupling may even be stronger [ $\lambda = 0.147 N(E_F)$ ] than calculated by Antropov *et al.*<sup>6</sup> In this case we determine even smaller  $N(E_F)$  values from our data [ $N(E_F) = 5.3$  states/eV spin  $C_{60}$  and  $N(E_F) = 5.9$  states/eV spin  $C_{60}$  for  $Rb_3C_{60}$ ] and  $\lambda$  increases from  $\sim 0.5$  to  $\sim 0.8$ . At this stage it is unclear whether the above discrepancies represent fundamental problems or whether they are caused by uncertainties in the calculations. Gunnarsson *et al.*<sup>25</sup> point out that small errors in the phonon eigenvectors can have a large effect on the electron-phonon coupling strength. Further, the calculated  $N(E_F)$  values depend strongly on the underlying orientational ordering of the  $C_{60}$  molecules in the  $A_3C_{60}$  phases

and idealized structures have been used in the calculations,<sup>6</sup> whereas the x-ray diffraction experiments have been interpreted in terms of random disorder.<sup>26</sup>

Since  $K_3C_{60}$  and  $Rb_3C_{60}$  are isostructural, important information can be obtained by a comparison of their respective density of states. The ratio  $\epsilon = N(E_F)_{Rb_3C_{60}}/N(E_F)_{K_3C_{60}}$  (and the ratio of the associated  $\lambda$ 's) depends strongly on the frequency of the phonons involved in the pairing mechanism,<sup>27</sup> and the ratio found from the present work,  $\epsilon = 1.13 \pm 0.24$ , supports the scenario that the electrons are coupling to high-frequency intramolecular phonons ( $\epsilon \sim 1.69$  is expected for low-frequency intermolecular phonon coupling<sup>22</sup>). This is in agreement with the experimental results of Sparn *et al.*<sup>7</sup> ( $\epsilon = 1.11$ – $1.24$ ) and also with theoretically derived values for  $N(E_F)$  using electronic band structure calculations, which give  $\epsilon \sim 1.18$  (Ref. 27).

In conclusion, thermal expansion data of the superconducting fullerenes  $K_3C_{60}$  and  $Rb_3C_{60}$ , obtained via high-resolution dilatometry, provide important information for analyzing the superconducting state. The ratio of the specific heat discontinuities  $\Delta c_p(T_c)$  at  $T_c$ , derived from these data using the Ehrenfest relation (and thus the ratio of the calculated  $N(E_F)$  values), favor a pairing mechanism in which high-frequency intramolecular phonons are involved. The densities of states  $N(E_F)$  obtained from the present analysis are smaller than the ones found by numerous experimental estimates and are lying at the bottom end of the range of theoretically calculated values.

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