

Low-temperature specific heat of the graphite intercalation compounds KC_8 , CsC_8 , RbC_8 , and their parent highly oriented pyrolytic graphite

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The specific heat of the graphite intercalation compounds KC_8 , CsC_8 , and RbC_8 and their parent material, highly oriented pyrolytic graphite (HOPG), has been determined between 0.48 and 90 K. The results are analyzed in terms of electronic and lattice contributions. The electronic contribution to the specific heat of these compounds is enhanced by at least 29 times above that for HOPG. Comparisons are made to theoretical band-structure calculations. The lattice contribution shows deviations from a Debye model for $T > 5$ K, which can be mathematically fitted by an Einstein specific-heat function. While our results for RbC_8 are unique, comparison with previous results for powder-based KC_8 and CsC_8 samples over a limited temperature range suggest that the type of parent graphite and/or details of preparation technique may influence the physical properties of these compounds.

I. INTRODUCTION

We have determined the specific heat C_p of the alkali-metal graphite intercalation compounds KC_8 , CsC_8 , and RbC_8 and their parent material, highly oriented pyrolytic graphite (HOPG) between 0.48 and 90 K. This is the first reported measurement of RbC_8 and considerably extends the temperature range of previous measurement (limited to 1.5–5 K) of C_p for KC_8 and CsC_8 made by Mizutani, Kondow, and Massalski (MKM).¹

While the phenomenon of graphite intercalation has been known since 1841,² recent interest has centered on the two-dimensional behavior of intercalation compounds, which results in highly anisotropic electrical properties. Intercalation increases the in-plane conductivity of graphite and, in one case, room-temperature conductivities comparable to that of copper were reported.³

An intercalation compound of graphite consists of layers of carbon between intercalant layers, the number of layers of carbon determining the stage of the compound. Hence, a stage-1 material consists of alternating layers of carbon and intercalant, as in KC_8 , CsC_8 , and RbC_8 . In addition, in a stage-1 compound, the intercalant layers are close-packed and have no vacancies, as must occur in second- and higher-stage compounds such as KC_{24} , CsC_{24} , etc.⁴

Measurement of the low-temperature specific heat C_p provides information on the electronic density of states at the Fermi level, $N(E_F)$, and, through knowledge of the lattice contribution to C_p , at least qualitative information on the phonon spectrum, enabling comparison with recent theo-

retical models. A rigid-band model has been proposed by Dresselhaus *et al.*,⁵ while Inoshita *et al.* have calculated the band structure of KC_8 using the tight-binding method and the extended Hückel approximation.⁶ Our results are compared with these models.

Theoretical calculations of $N(E_F)$ do not include electron-phonon effects. The ratio of the theoretical to the experimental value of $N(E_F)$ gives a value for the electron-phonon enhancement factor λ , which, together with $N(E_F)$, can be related to the onset of superconductivity. Superconductivity was initially reported by Hannay *et al.*⁷ at 0.135 K for CsC_8 , 0.151 K for RbC_8 , and 0.39 K for KC_8 , while more recent measurements reported a T_c of 0.128 to 0.198 K for KC_8 .⁸ As may be expected, we observed no evidence of superconductivity in C_p down to 0.48 K in any of the three materials.

II. EXPERIMENTAL

To determine the specific heat of these air-sensitive compounds, we used a modification of an existing calorimetry cryostat.^{9,10} Because the samples were air sensitive, they were mounted within a removable calorimeter inside a high-purity nitrogen-atmosphere glove box. The removable calorimeter was sealed full of nitrogen, and the gas was pumped out when the calorimeter had been transferred to and cooled within the cryostat to about 150 K. Use of the removable calorimeter prevented our using a conventional heat switch and necessitated the development of a modification of a thermal-relaxation technique for determination of C_p .^{11,12} This technique requires exponential, rather than linear, extrapola-

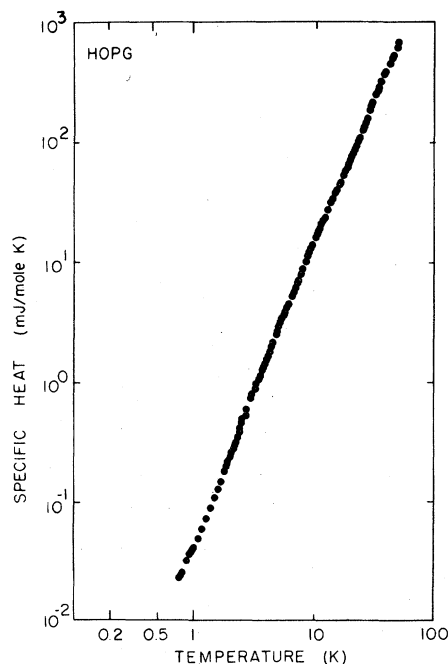


FIG. 1. C_p as a function of T on log-log coordinates for HOPG.

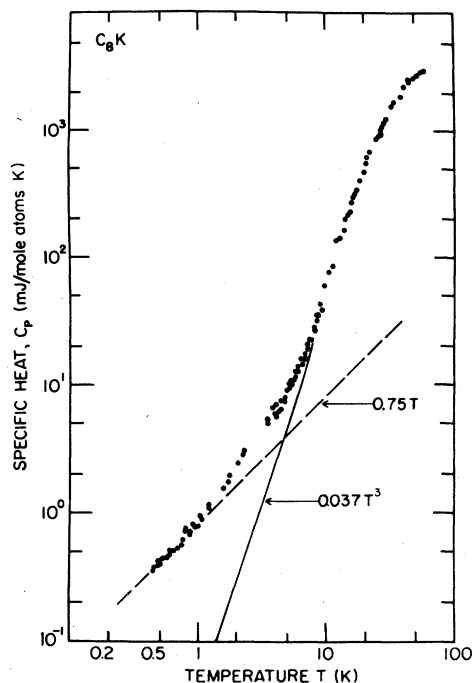


FIG. 2. C_p as a function of T on log-log coordinates for KC_8 . The solid line represents the lattice contribution and the dotted line the electronic contribution.

tion of temperature drifts.

The addenda we used consisted of two small sapphire plates between which the sample was held. One plate was stationary, mounted on Teflon-tipped copper posts, while the other plate was placed on the sample and held down by a Teflon-tipped copper screw. To measure temperature, we used two carbon resistance thermometers, Spear 470 and Spear 820 (Ref. 13) attached to one addenda plate with epoxy. The heater was also a carbon resistor mounted on the other plate. The thermometers were calibrated during each data run using small amounts of exchange gas. From 0.4 to 1.5 K, calibrations were made against the vapor pressure of ^3He corrected for thermomolecular effects.¹⁴ Above 1.5 K, the reference standards were calibrated germanium resistors.¹⁵

Our samples were made from single pieces of HOPG (Ref. 16) and all were 0.5 to 1.5 grams in mass. They were prepared using the two-bulb method in a temperature-controlled two-zone furnace.¹⁷ Samples were removed from the furnace when they showed the golden color and expansion characteristic of stage-1 compounds. Mass was also measured to determine that the increase was that expected for stage 1. Color was tested by random cleaving to make certain that it was the same throughout the samples. Samples made by identical techniques have been x-rayed

to identify the stage.¹⁸

We are reporting values of C_p . Correction to a theoretical C_v will be possible when information on the physical properties in the correction term is available.

In presenting our results, we state numbers based on two different molecular formula units. For comparison with theoretical calculations and results for graphite, we use the formula $M_{1/8}C$, where M is K, Cs, or Rb. The molecular weight of a sample is then given by $\frac{1}{8}$ (atomic weight of M) + atomic weight of C. This gives specific heat in mJ/mole of carbon K. For comparison with previous results of MKM, we use their formula unit, MC_8 . The resulting molecular weight is $[8 (\text{atomic weight of C}) + \text{atomic weight of } M]/9$, which gives specific heat in mJ/mole of atoms K. Thus, the two specific heats are related by $C_p (\text{mJ/mole C K}) = \frac{8}{9} C_p (\text{mJ/mole atoms K})$. All data presented in Figs. 1, 2, and 3 is given in terms of mJ/mole atoms K.

III. RESULTS AND ANALYSIS

The data of C_p versus T for the parent HOPG, KC_8 , RbC_8 , and CsC_8 are shown in Figs. 1, 2, 3, and 4, respectively, using log-log scales to encompass the wide range of temperature and value

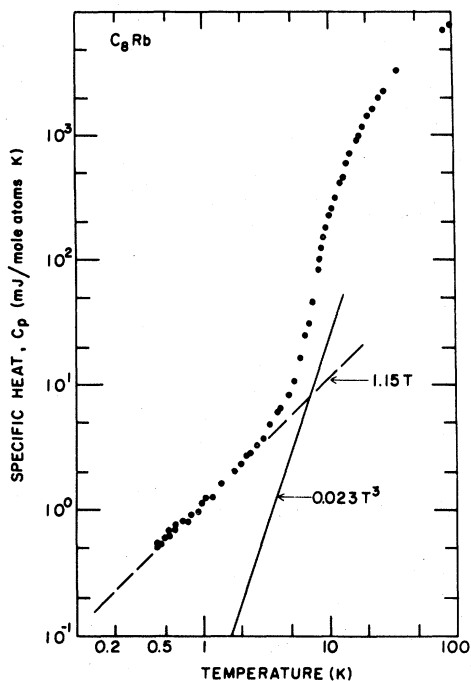


FIG. 3. C_p as a function of T on log-log coordinates for RbC_8 . The solid line represents the lattice contribution and the dotted line the electronic contribution.

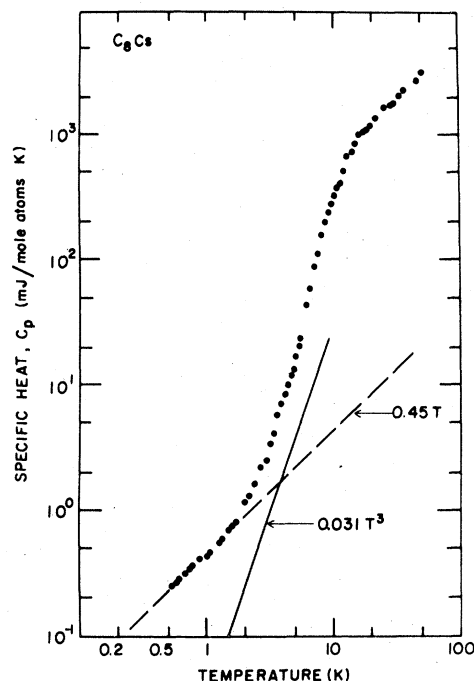


FIG. 4. C_p as a function of T on log-log coordinates for CsC_8 . The lattice contribution is shown by a solid line and the electronic contribution by a dotted line.

of specific heat and to readily show the variations of dependence of C_p on powers of T in the various temperature regions as discussed below.

Our analysis of C_p was carried out in terms of two contributions:

$$C_p = C_E + C_L, \quad (1)$$

where C_E is the electronic contribution (γT), which is determined by the electronic density of states at the Fermi level, $N(E_F)$, and the electron-phonon enhancement factor λ since¹⁹

$$\gamma = \frac{1}{3} \pi^2 k^2 (1 + \lambda) N(E_F). \quad (2)$$

The values of γ for the four materials are given in Table I together with a density of states calculated assuming $\lambda = 0$. A value of λ can be obtained from comparison with theoretical calculations of

$N(E_F)$ as we discuss below.

Below about 4 K the lattice contribution C_L can be described by $\beta(0)T^3$, where the low-temperature limit of the Debye temperature $\Theta_D(0)$ is obtained from

$$\Theta_D(0) = \left(\frac{1.944 \times 10^6 \text{ mJ/mole K}}{\beta(0)} \right)^{1/3}. \quad (3)$$

Resulting values of $\beta(0)$ and $\Theta_D(0)$ for the intercalated compounds are given in Table II, where they are compared with previous results of MKM. Above about 5 K, C_L deviates rapidly from the T^3 contribution expected for a Debye solid up to $\Theta_D(0)/10$ (~40 K for these materials), except in the case of KC_8 . To exhibit the behavior of C_L for the intercalated compounds above 5 K we have plotted C_L/T^3 vs T , as shown in Fig. 5.

TABLE I. Electronic specific-heat parameters.

Sample	γ ($\frac{\text{mJ}}{\text{mole of C K}^2}$)	$N(E_F)$ ($\frac{\text{states}}{\text{eV atom of C}}$)	γ ($\frac{\text{mJ}}{\text{mole atoms K}^2}$)	$N(E_F)$ ($\frac{\text{states}}{\text{eV atom}}$)	γ^a ($\frac{\text{mJ}}{\text{mole atoms K}^2}$)
RbC_8	1.3 ± 0.01	0.55	1.15 ± 0.01	0.49	
CsC_8	0.51 ± 0.01	0.22	0.45 ± 0.01	0.19	0.63
KC_8	0.84 ± 0.01	0.35	0.75 ± 0.01	0.32	0.697 ± 0.006

^aValues of MKM (Ref. 1).

TABLE II. Lattice parameters calculated per mole of atoms.

Sample	$\beta(0)$ (mJ/mole K ⁴)	$\Theta_D(0)$ (K)	$\beta(0)^a$	$\Theta_D(0)^a$
RbC ₈	0.023 ± 0.001	439 ± 6		
CsC ₈	0.031 ± 0.001	397 ± 4	0.049	341
KC ₈	0.037 ± 0.001	374 ± 4	0.1502 ± 0.0013	234.8 ± 0.7

^aValues of MKM (Ref. 1).

IV. DISCUSSION

A. Highly oriented pyrolytic graphite: HOPG

The specific-heat values for the parent HOPG are shown in Fig. 1 and the analyzed values of γ , $\beta(0)$, and $\Theta_D(0)$ are given in Table III, where they are compared with previous values for natural Madagascar graphite²⁰ and spectroscopic powder.¹ In Fig. 1 the small linear contribution is barely apparent. We note that the value of γ for our HOPG is closer to that of natural Madagascar graphite than is the same parameter for the powdered graphite used by MKM. The lattice contribution C_L of our HOPG varies as T^3 only at the lowest temperatures, tending towards a $T^{2.3}$ behavior above about 10 K. This behavior is consistent with theoretical discussions,²¹ which attribute the lower power dependence at higher temperatures to the predominantly two-dimensional phonon spectrum. The $\Theta_D(0)$ values for the three graphites listed in Table III agree closely.

B. KC₈, RbC₈, and CsC₈

1. Electronic specific heat

The electronic contribution to the specific heat ($C_E = \gamma T$) is enhanced by at least a factor of 29 above the value for HOPG in these three stage-1 compounds. The values of γ obtained are listed in Table I in units of mJ/mole of C K and in units of mJ/mole of atoms K and the linear contributions are indicated in Figs. 2, 3, and 4. The values of γ are different for each compound, highest in RbC₈ and lowest in CsC₈. This is in contrast to the results of MKM, who found the values of γ for KC₈ and CsC₈ to be within 10% of each other. Their values are also listed in Table I. Our result for KC₈ agrees fairly closely with that of MKM, while the values for CsC₈ differ by 29%. Our value of γ for RbC₈ is at present unique.

That the experimental values of γ are different for each compound is not surprising for several reasons. The intercalants differ considerably in

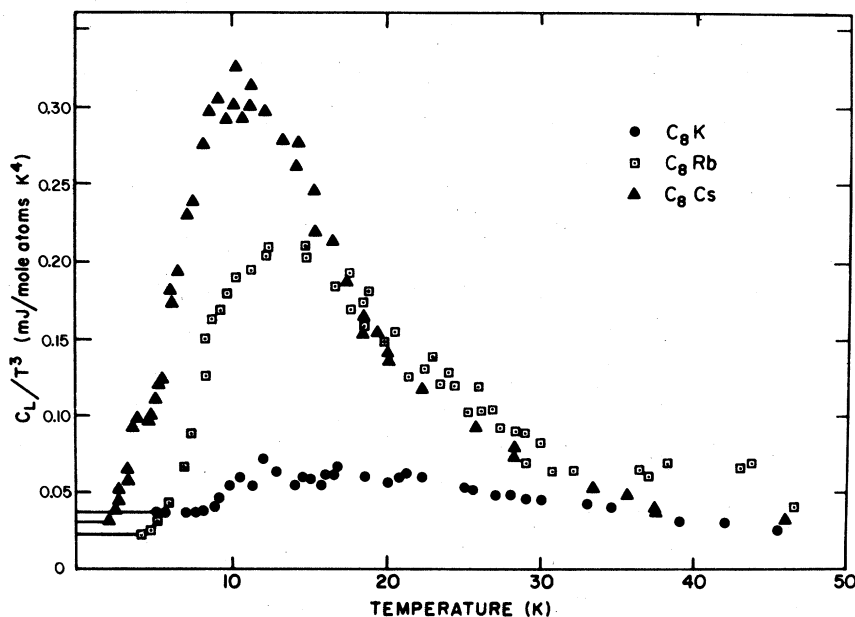
FIG. 5. C_L/T^3 as a function of T for KC₈, CsC₈, and RbC₈.

TABLE III. Low-temperature specific-heat coefficients of several forms of graphite.

	γ (mJ/mole K ²)	$\beta(0)$ (mJ/mole K ⁴)	$\Theta_D(0)$ (K)
HOPG	0.0173	0.0249	427
Natural Madagascar graphite ^a	0.0138	0.0277	413
Spectroscopic powder ^b	0.03 ± 0.01	0.026 ± 0.001	421 ± 4

^a J. C. van der Hoeven, Jr. and P. H. Keesom, Ref. 20.

^b MKM, Ref. 1.

size and, consequently, the *c*-axis expansion occurring upon intercalation varies between compounds. In addition, the intercalant layer stacking sequence differs, at least between KC₈ [$\alpha\beta\gamma\delta\alpha$ (Ref. 4)] and CsC₈ [$\alpha\beta\gamma\alpha$ (Ref. 4)]. Further, it is known that the stacking sequence in RbC₈ can be modified by heat treatment. It is close to $\alpha\beta\gamma\delta\alpha$ when synthesized at the temperatures we used, but only becomes perfect $\alpha\beta\gamma\delta\alpha$ after additional heating.²²

Two theoretical models have recently been used to determine $N(E_F)$ in these intercalation compounds. The rigid-band approach, proposed by Dresselhaus *et al.*⁵ and also used by MKM gives values of $N(E_F)$ in reasonable agreement with experiment for stage-2-4 compounds, but underestimates $N(E_F)$ for stage 1. Inoshita *et al.*⁶ used a tight-binding approximation to determine $N(E_F)$ for KC₈ obtaining 0.27 states/eV carbon atom, which corresponds to a theoretical γ of 0.64 mJ/mole of carbon K². This value of γ , although about 24% below our experimental value for KC₈, is 25% higher than our value for CsC₈. Such a comparison between alkali metals may reflect the difference in stacking sequences referred to above.

A true comparison of experimental (γ_{expt}) and theoretical (γ_{theor}) values must also take into account the electron-phonon enhancement factor λ , which relates the two by

$$\gamma_{\text{expt}} = \gamma_{\text{theor}} (1 + \lambda). \quad (4)$$

We may then calculate λ using Eq. (4) only for KC₈ since theoretical calculations for RbC₈ and CsC₈ have not been made. We obtain $\lambda = 0.3$ assuming Inoshita's value of $N(E_F)$. Comparative values of λ can be obtained from very high temperature resistivity studies,²³ but these are probably not possible with these compounds due to deterioration or stacking sequence changes at high tem-

peratures. Alternatively, the existence of superconductivity in KC₈, RbC₈, and CsC₈ provides a value of λ . Using the McMillan equation,²⁴ we can determine λ knowing $\Theta_D(0)$, the superconducting transition temperature T_c , and the Coulomb repulsive constant μ^* (assumed to be 0.1):

$$\lambda = \frac{1.04 + \mu^* \ln(\Theta_D/1.45T_c)}{(1 - 0.62\mu^*) \ln(\Theta_D/1.45T_c) - 1.04}. \quad (5)$$

Hannay *et al.* reported a T_c for KC₈ of 0.55 K, but described this sample as "wet" with excess metal. A stoichiometric sample was reported by them to have a $T_c = 0.39$ K. The transition temperatures for presumably stoichiometric RbC₈ and CsC₈ were reported to be 0.151 and 0.135 K, respectively. These samples were all based on "pyrolytic graphite." We observed no anomaly in the specific heat of these three compounds down to 0.48 K, suggesting that transition temperatures for stoichiometric samples based on HOPG are below this temperature. Recently, Koike *et al.*⁸ reported a T_c for KC₈ of only 0.128 to 0.198 K, depending on the sample, for HOPG-based compounds. In contrast, a value of $T_c = 0.08$ K was obtained by Kobayashi and Tsujikawa²⁵ for KC₈ made from powdered graphite. Using our value of Θ_D and the average of Koike's values for T_c and assuming $\mu^* = 0.1$ in Eq. (5), we find $\lambda = 0.3$ again, in agreement with the comparison of γ_{expt} and γ_{theor} .

Comparison of our specific-heat results for HOPG-based samples with those of MKM for powder-based samples combined with the varying results just quoted for T_c strongly suggests that the physical properties of these compounds are dependent upon the nature of the parent graphite, the physical properties of which have already been shown to be source dependent (Table III, Refs. 20 and 21). Inoshita *et al.*, in applying the McMillan equation [Eq. (5)] to determine μ^* from physical properties known at the time, combined Θ_D and γ_{expt} (to determine λ) obtained for powder KC₈ with a T_c for "wet" KC₈ made from pyrolytic graphite. Their result ($\mu^* = -0.01$) was thought unreasonable. We find, however, that using values of T_c and Θ_D for KC₈ made consistently from HOPG or from powder and the respective values of λ from Eq. (4), we obtain μ^* values between 0.1 (HOPG based) and 0.04 (powder based), which are physically reasonable, being comparable to the typically quoted value of 0.1. This suggests that the McMillan equation may be applicable to these compounds even though it was originally derived for niobium. Extending this discussion to RbC₈ and CsC₈ is not possible at present since there are no theoretical values of $N(E_F)$ from which to estimate λ .

A recent study²⁶ of the valence bands of pure

graphite, KC_8 , RbC_8 , and CsC_8 by ultraviolet photoemission spectroscopy found that the shift of the Fermi level of the compounds compared to that of graphite is highest for RbC_8 and lowest for CsC_8 . This sequence is similar to our finding that RbC_8 has the highest γ value of the three compounds and CsC_8 has the lowest.

2. Lattice specific heat C_L

We note in Sec. III that C_L for these three compounds below about 5 K could be described by the low-temperature approximation of the Debye lattice model and the resulting values of $\Theta_D(0)$ are given in Table II. The values obtained for our samples are higher and closer to those of their parent graphite than are the values of MKM. The difference between our values and those of MKM is most marked in the case of KC_8 , while our value for RbC_8 is unique. It is possible that the difference between our values and those of MKM is due to the sample form (HOPG versus powder), but further comparative measurements will be needed to verify this point.

We see from Fig. 2 that C_p for KC_8 continues with a slope very close to 3 above 5 K as would be expected from the Debye model, while in the same temperature region the slopes of the C_p vs T graphs for RbC_8 (Fig. 2) and CsC_8 (Fig. 3) approach values of 4 to 5. This difference in behavior is emphasized in Fig. 5 where we plot C_L/T^3 vs T for the three compounds. For an ideal Debye solid such a plot would result in a horizont-

al line at $C_L/T^3 = \beta(0)$ up to about $\Theta_D(0)/10$ (about 40 K) and we see that in the case of KC_8 the deviation from such a temperature dependence is quite small. For CsC_8 and RbC_8 the deviation is very marked. In the case of CsC_8 , this was attributed to a Schottky anomaly or an Einstein mode by MKM. Specific-heat measurements below 5 K cannot distinguish between these two forms since, mathematically, the low-temperature approximations of these functions are the same.

The appropriate parameters for Schottky and Einstein models were found by subtracting γT and $\beta(0)T^3$ from C_p between 4 and 10 K and fitting the result to the common low-temperature approximation, of the general form

$$CT^2 = Ae^{-B/T}, \quad (6)$$

where A determines the oscillator strength and B the excitation energy. Using the full expression for each possible contribution,

$$C_{\text{Ein}} = 3nR \frac{T_E^2}{4T^2} \text{csch}^2\left(\frac{T_E}{2T}\right) \quad (7)$$

and

$$C_{\text{Sch}} = nR \frac{\delta^2}{T^2} \frac{g_0}{g_1} \frac{\exp(\delta/T)}{[1 + (g_0/g_1)\exp(\delta/T)]^2}, \quad (8)$$

we plot the resulting values of $[C_{\text{Ein}}/T^3 + \beta(0)]$ and $[C_{\text{Sch}}/T^3 + \beta(0)]$ vs T for temperatures up to 50 K in Figs. 6 and 7. In Eqs. (7) and (8), n is the fraction of atoms contributing to the anomaly, T_E is the Einstein temperature, R is the universal gas con-

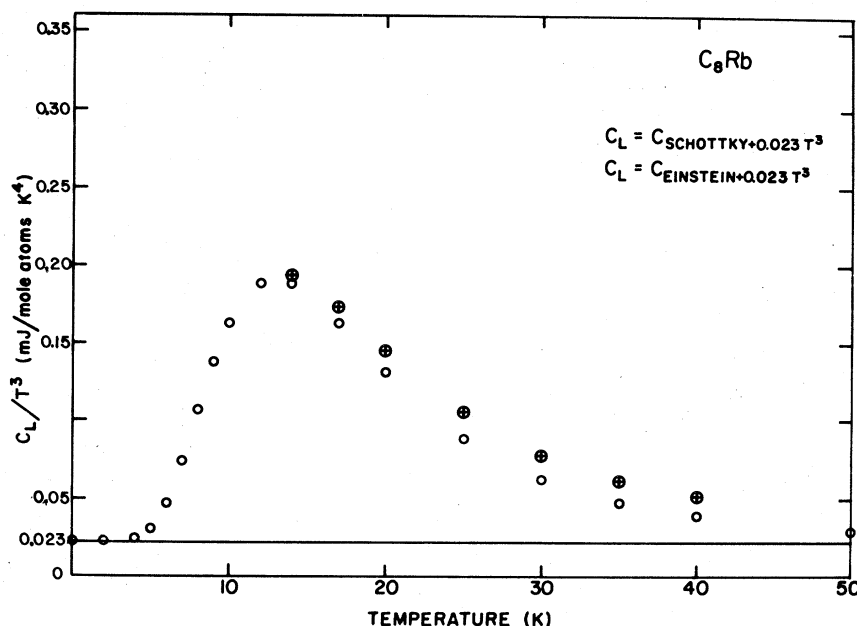


FIG. 6. C_{Sch}/T^3 and C_{Ein}/T^3 as functions of temperature using parameters for RbC_8 .

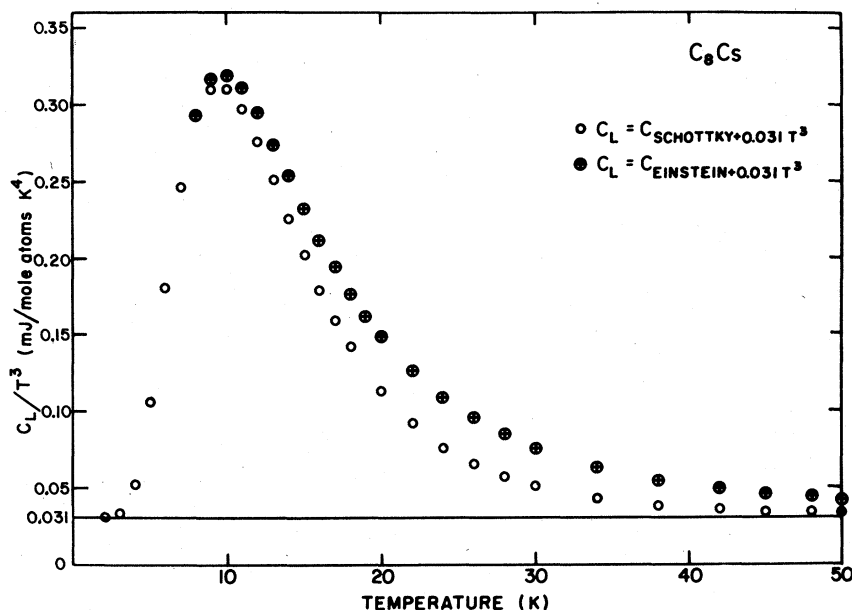


FIG. 7. C_{Sch}/T^3 and C_{Ein}/T^3 as functions of temperature using parameters for CsC_8 .

stant, g_0 and g_1 the degeneracies of the ground and first excited energy levels, and δ the energy-level splitting. It can be seen from these graphs that $C_{Ein} = C_{Sch}$ up to about 8 K for CsC_8 and 14 K for RbC_8 , then the two models begin to deviate, with the Einstein fit being somewhat closer to the actual data shown in Fig. 5. We conclude that an Einstein model provides the best mathematical fit to these anomalies, within the limits of our analysis. The appropriate mathematical parameters for Eq. (7) are given in Table IV where they are compared with the values obtained by MKM. From this table we note that the values of δ agree for CsC_8 while the value of n is larger in our CsC_8 and much larger for RbC_8 .

The physical origin of these contributions to C_L in CsC_8 , RbC_8 , and other intercalation compounds¹ is not yet understood, particularly in view of their apparent singular absence in KC_8 . There are, however, important distinctions between the structure of KC_8 and the structure of RbC_8 and CsC_8 .

which may alter the lattice contribution to the specific heat, possibly adding extra discrete vibrational modes. The core radius of potassium is such that it will fit into the graphite structure with the ideal interlayer spacing proposed by Rudorff and Schulze.⁴ It is also known to have an $\alpha\beta\gamma\delta$ interlayer sequencing. On the other hand, the ion core radius of rubidium is 4% too large and that of cesium is 19% too large for the ideal structure. In addition RbC_8 is known to change its interlayer structure from $\alpha\beta\gamma$ to $\alpha\beta\gamma\delta$ under appropriate heat treatment⁴ and CsC_8 is known to be $\alpha\beta\gamma$ at room temperature. Thus RbC_8 and CsC_8 are potentially less well ordered than KC_8 . This lack of perfect ordering may permit low-lying phonon modes to exist. These could contribute to the specific heat as Schottky-type anomalies or Einstein modes. It has already been suggested that perturbation of graphite lattice modes by the intercalant may be the source of the "anomalies."²²

The difference in sizes between the specific-heat data we obtained and that obtained by MKM suggests that the details of heat treatment, cooling rate, and other factors in the preparation of samples, as well as the nature of the parent graphite, determine the extent of disorder in the sample and, thus, may influence the total specific heat. Studies of the effects of preparation technique and graphite type on the physical properties of intercalation compounds certainly appear necessary.

TABLE IV. Einstein specific-heat parameters.

Sample	T_E (K)	n	T_E^a	n^a
RbC_8	65 ± 1	0.088		
CsC_8	48 ± 1	0.060	47.6 ± 1.0	0.042

^aValues of MKM (Ref. 1).

V. SUMMARY

The specific heat C_p of our HOPG-based samples of KC_8 , RbC_8 , and CsC_8 in the temperature range between 0.48 and 90 K can be analyzed in terms of electronic and lattice contributions. The electronic contribution is different for each of the compounds, but is at least 29 times greater than in the parent HOPG. It is also greater than the predictions of theoretical models to date, though the difference may be due to electron-phonon enhancement, which has not been completely treated theoretically. The lattice contribution provides low-temperature limits to Θ_D which are not more than 70 K below the value for HOPG. Above about 5 K, CsC_8 and RbC_8 show a large increase in specific heat over that of KC_8 . While the physical source of this is not yet known, it can be described mathematically by an Einstein specific-heat function.

Our results agree with the general pattern of those of MKM, which were obtained for graphite powder based KC_8 and CsC_8 over a much narrower temperature range, but disagree numerically. This suggests strongly that the form and

nature of the parent graphite and/or fine details of the preparation techniques may influence physical properties of the resulting intercalation compounds. Further studies of these compounds and higher-stage compounds are currently in progress.

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