

Low-temperature specific heats of rubidium-graphite intercalation compounds

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The low-temperature specific heats of graphite-rubidium intercalation compounds were measured using a conventional calorimetric method in the temperature range from 1.5–6 K. The specific heats consisted of the electronic and lattice specific heats as well as a specific-heat anomaly due to a dispersionless optical mode of lattice vibration involving rubidium atoms. The present as well as previous data for graphite-potassium and -cesium compounds can be explained in terms of the heterogeneous charge distribution along the c axis of the compounds.

I. INTRODUCTION

The electronic structures of graphite intercalation compounds have been extensively studied because of their interesting physical and chemical properties¹ related to several practical applications.² We previously reported the low-temperature specific-heat measurements of the graphite intercalation compounds with potassium and cesium (C_xK and C_xCs).³ For the lower-stage alkali compounds ($x \leq 24$), the coefficient of electronic specific heat, γ , obtained can be explained in terms of the rigid band model based on pure graphite. However, recent experimental and theoretical studies^{4,5} favor heterogeneous charge distribution along the c axis of the intercalation compounds. This heterogeneous distribution is not compatible with the use of the rigid band model, since the latter implicitly requires a homogeneous charge distribution. For C_8K , the γ value previously obtained agrees reasonably well with the theoretical prediction based on a tight-binding approximation⁶ assuming a reasonable value of the electron-phonon enhancement factor. However, the more sophisticated calculation⁷ requires an enhancement factor that is too large in order to match the theoretical and experimental values.

In addition, we reported previously that the Debye temperatures depend on the concentration of alkali metals in the compound.³ There appears to be a systematic trend in the dependence of the alkali metal concentration. In the case of C_xCs , we discovered a dispersionless optical phonon which introduces an anomaly in the low-temperature specific heats.³ C_xK compounds do not exhibit the anomaly, probably because the characteristic frequency of the optical phonon is too large to make a sizable contribution to the specific heats. The

characteristic frequency and the intensity of the anomaly depend also on the concentration of cesium atoms in the compound. The acoustical- and optical-phonon behavior may be understood in terms of the charge distribution along the c axis of these lamellar compounds. Rubidium compounds (C_xRb) require study in order to confirm that the behavior found for C_xK and C_xCs compounds are common to all graphite-alkali metal intercalation compounds.

We report here measurements of low-temperature specific heats of C_xRb in order to confirm the validity of our previous measurements and to analyze the data within the framework of nonuniform charge distribution along the c axis of these compounds.

II. EXPERIMENTS

Spectroscopic graphite powder, SP-1, produced by Union Carbide Corp. was intercalated with rubidium in a sealed Pyrex tube using the dual furnace method for first- and second-stage compounds.³ Third- and fourth-stage compounds were produced by diluting the first-stage compound with the necessary amount of graphite. Each sample thus synthesized was annealed at 300 °C for about three days. The sample, sealed in the Pyrex tube, was transferred and compacted into a gold-plated copper container with a Teflon-sealed lid in an argon atmosphere. Transfer was accomplished in a well-controlled dry box through which circulated pure argon gas. The presence of argon gas had no effect on the measurements of the low-temperature specific heats as described elsewhere.³

The total weight of the sample was approximately 5 g as listed in Table I. The 18-g gold-plated container was 45 mm deep and had an inner diameter of 10 mm. The heat-capacity measurements were made in a conventional calorimeter in the temper-

TABLE I. Low-temperature specific-heat coefficients in C_xRb compounds.

Sample	Molar weight (g)	Weight (g)	γ (mJ/mol K ²)	α (mJ/mol K ⁴)	Θ_D (K)	Δ (K)	A
C_8Rb	20.173	4.719	0.646 ± 0.002	0.0410 ± 0.0002	361.9 ± 0.6	71 ± 1	0.8 ± 0.1
$C_{24}Rb$	14.949	4.697	0.255 ± 0.001	0.0510 ± 0.0001	336.5 ± 0.2	51 ± 1	0.070 ± 0.008
$C_{36}Rb$	13.996	4.662	0.192 ± 0.001	0.0440 ± 0.0002	353.5 ± 0.5	51 ± 1	0.057 ± 0.006
$C_{48}Rb$	13.510	4.837	0.143 ± 0.001	0.0376 ± 0.0001	372.5 ± 0.3	51 ± 1	0.042 ± 0.004

ature range between 1.5 and 6 K. The thermometer used was a well-calibrated germanium resistor which was embedded in the hole on the container. The thermal response to the applied heat was always sufficiently rapid to ensure accurate and reproducible data. Each experiment involved three to four runs involving more than 200 data points over the temperature range studied.

III. RESULTS

The ratio of the low-temperature specific heats, C , of C_xRb to the temperature, T , are plotted against T^2 in Fig. 1. The molar quantity for C_xRb is defined as $(xA_C + A_{Rb})/(x + 1)$, where A_C and A_{Rb} represent the atomic weights of carbon and rubidium, respectively. As seen in Fig. 1, the data points tend to deviate from linearity with increasing temperature. The specific heat can consequently be expressed as

$$C = \gamma T + \alpha T^3 + \Delta C. \quad (1)$$

The terms γT and αT^3 represent the electronic and lattice specific heats of C_xRb , respectively, and the Debye temperature Θ_D was calculated from the coefficient α . In addition, the coefficient γ provides the density of states at Fermi level. The additional term, ΔC , was found to follow the relation

$$\Delta C = A'(\Delta/T)^2 \exp(-\Delta/T). \quad (2)$$

The characteristic temperature Δ and the coefficient A' were determined by the linear relation between $\ln(\Delta C T^2)$ and $1/T$. The parameters γ , α , Δ , and Θ_D thus obtained are listed in Table I. Similar temperature dependence is reported³ for the graphite intercalation compounds of cesium.

IV. DISCUSSION

In a previous report,³ we explained the electronic specific heats of C_xK and C_xCs , except for first-stage compounds, in terms of a graphite rigid band and assuming complete ionization of alkali metal atoms. The results of Suematsu *et al.*⁸ for the de Haas-van Alphen effect in $C_{48}Rb$ have been accounted for using a folded Brillouin zone of pure graphite because of the existence of super lattices along the c axis of the compound, where a homo-

geneous charge distribution along the c axis is implicitly assumed. It should be emphasized that they indicate that the volume of the Fermi surface determined by this experiment gives a much lower electron density than that calculated by assuming complete ionization of the alkali metal atoms.

On the other hand, there are several experimental results indicating heterogeneous charge distribution along the c axis. Solin *et al.* and M.S. Dresselhaus *et al.* have found in Raman scattering measurements that there are two different types of carbon layers in compounds having stage numbers $n \geq 3$, namely, the carbon layers adjacent to the alkali metal layers and the other not adjacent to any alkali metal layers.⁴ Pietronero *et al.* have calculated the charge distribution along the c axis of an acceptor-type compound on the basis of a simplified crystal structure.⁵ The charge density is found to fall off so rapidly that carbon layers, one layer removed from the intercalant layers, possess no noticeable charge. An attempt will be made to establish which model is adequate for explaining the present results.

A. Electronic specific heats

In Fig. 2, the γ coefficients for C_xRb are plotted against the metal-atom concentration, with the

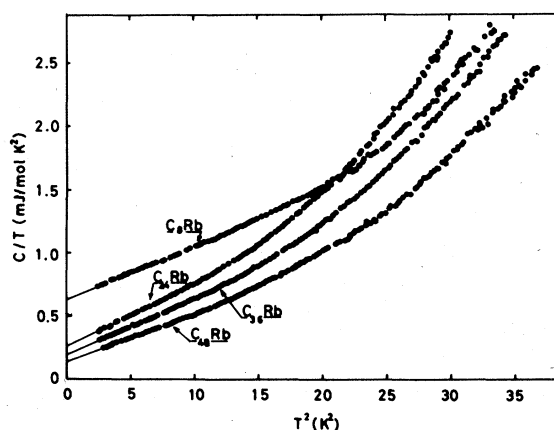


FIG. 1. C/T vs T^2 plots for the rubidium-graphite intercalation compounds in the temperature range from 1.5 to 6 K.

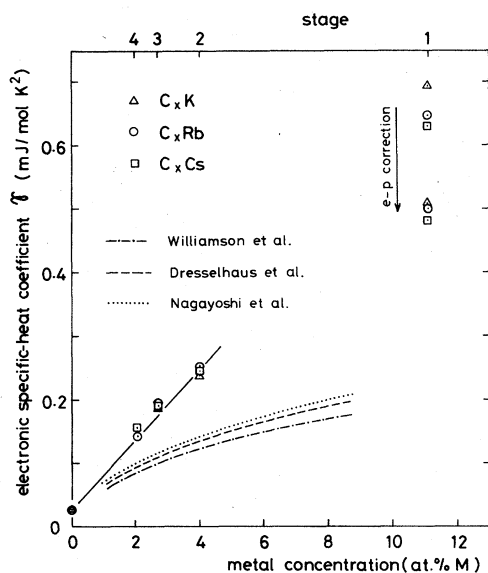


FIG. 2. The electronic specific-heat coefficients γ are shown as a function of alkali-metal-atom concentration. The data for C_xK and C_xCs compounds are taken from a previous report (Ref. 3). All lines, excepting the solid straight line, refer to theoretical predictions based on the rigid-band model of pure graphite. The solid straight line is obtained on the basis of the heterogeneous charge-distribution model.

results previously reported for C_xK and C_xCs also included. The values of γ are found to be almost independent of the intercalant species. This behavior verifies the previous postulation that the electronic structure of these compounds is determined by the distribution of the valence electrons transferred from the alkali metal atoms over the carbon layers.

Since the first-stage compound C_8Rb exhibits superconductivity below a transition temperature of 0.15 K,⁹ the electron-phonon coupling constant of C_8Rb is determined to be 0.30 using McMillan's equation.¹⁰ Here the Debye temperature used is the 361 K given in Table I, together with a Coulomb repulsion coefficient of 0.1. The experimental value of γ was corrected to be 0.50 mJ/mol K² on the basis of the equation

$$\gamma_{\text{corr}} = \gamma_{\text{exp}} / (1 + \lambda).$$

The corrected value γ_{corr} is shown in Fig. 2 as well as the corresponding values for C_8K and C_8Cs . The value of γ_{corr} thus derived agrees fairly well with the theoretical prediction of Inoshita *et al.*, which is 0.6 mJ/mol K².⁶ For second stage compounds, the experimental data exceed any values calculated using various energy bands for pure graphite assuming complete ionization of the alkali metals. The electron-phonon coupling would

reduce the apparent γ values determined experimentally and/or the density-of-states bands of pure graphite would be noticeably modified by the intercalation as is the case for first-stage compounds. Exact band calculations and the evaluation of the electron-phonon coupling are awaited in order to elucidate this discrepancy.

For higher-stage compounds, C_xM , there are two types of carbon layers, namely, those adjacent to a metal layer (C_b layers) and those surrounded only by other carbon layers (C_i layers). If the charge is uniformly distributed over these layers, the graphite rigid band could provide an adequate density of states at the Fermi level of C_xM and consequently the γ value. As reported previously, the prediction based on McClure's graphite band agrees fairly well with the present data. It should be noted, however, that recent measurements of the de Haas-van Alphen effect¹¹ and magnetoreflexion,¹² as well as energy-band calculations,¹³ result in γ values about half as large as the present results.

As mentioned previously, several recent experimental and theoretical studies support the heterogeneous rather than the homogeneous model. One may assume an extreme case in which the valence electron transferred from the alkali metal atoms is localized in the C_b layers. Then the γ coefficient for C_xM will be

$$\gamma_{C_xM} = 25M(\gamma_{C_b} - \gamma_{C_i}) + \gamma_{C_i},$$

where $M = 1/(1+x)$, and γ_{C_b} and γ_{C_i} are the electronic specific-heat coefficients of the C_b and C_i layers, respectively. Since the valence electrons lie only on the C_b layers in this case, γ_{C_b} and γ_{C_i} may be regarded as the coefficients of the second-stage compound, $\gamma_{C_{24M}}$, and of pure graphite, γ_G , respectively. Then the above equation becomes

$$\gamma_{C_xM} = 25M(\gamma_{C_{24M}} - \gamma_G) + \gamma_G. \quad (3)$$

The solid line which satisfies Eq. (3) is in agreement with the observed data obtained for higher-stage compounds (see Fig. 2).

This nonuniform charge distribution can also explain the Fermi-level shift for C_xCs determined from the photoelectron spectra (PES) of Pfluger *et al.*¹⁴ For these compounds with $x \geq 24$, the Fermi level is mainly determined by the C_b - M - C_b composite layers and may not be affected by the presence of the C_i layers. Accordingly, the Fermi levels for these compounds are almost the same, as demonstrated in the PES for C_xCs of Pfluger *et al.*¹⁴ The measurements of low-energy optical transitions¹⁵ and magnetoreflexion¹⁶ as well as Raman scattering⁴ show that the electronic structure of the C_i layers remains graphitic upon intercalation in agreement with the present results.

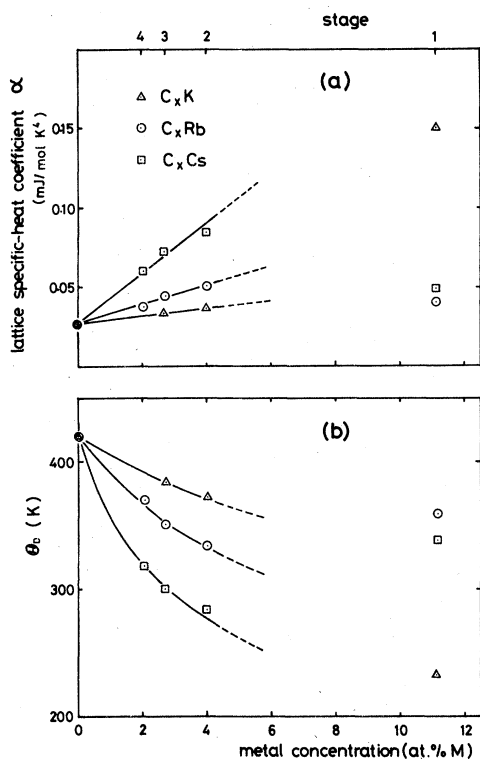


FIG. 3. (a) The lattice specific-heat coefficients α as a function of alkali-metal-atom concentration in various C_xM compounds. (b) The Debye temperatures θ_D calculated from α using the equation, $\alpha = (\frac{12}{5}) \pi^4 R \theta_D^{-3}$, as a function of alkali-metal-atom concentration in various C_xM compounds.

B. Lattice specific heats

Figures 3(a) and 3(b) show the plots of the lattice specific-heat coefficient α and the Debye temperature θ_D as a function of the alkali-metal-atom (M) concentration. The data for potassium and cesium compounds are from a previous report.³ As demonstrated in Fig. 3(a), α decreases linearly and approaches the value for pure graphite with decreasing M concentration except for first-stage compounds. The larger the atomic weight of M , the steeper the increment of the line. The dependence of α and θ_D on the concentration of M shows that the acoustic modes responsible for the term αT^3 must be related to lattice vibrations in which the alkali metal atoms, M , participate.

Except for first-stage compounds, the coefficient of the lattice specific heat for the compound C_xM , α_{C_xM} , on the basis of the heterogeneous model can be expressed as

$$\alpha_{C_xM} = \left(\frac{1}{1+x} \right) [25\alpha_{C_b} + 12\alpha_{C_t}(n-2)], \quad (4)$$

where α_{C_b} and α_{C_t} are the coefficients for the C_b

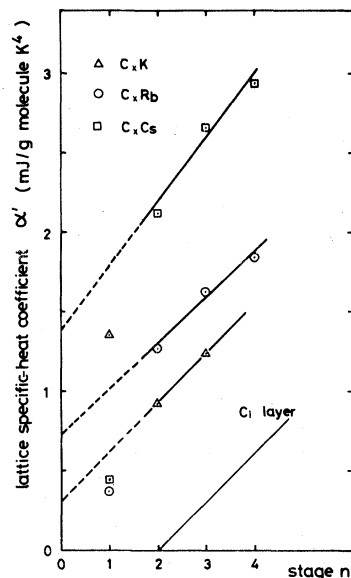


FIG. 4. The lattice specific-heat coefficients α'_{C_xM} in units of mJ/g molecule K^4 , are plotted against the stage number n for various C_xM compounds. The contribution to α from the C_t layers, which are assumed to be identical to the carbon layers in pure graphite, is indicated.

and C_t layers, respectively, and n refers to the stage number of C_xM . Figure 4 shows that $\alpha'_{C_xM} [(1+x)\alpha_{C_xM}]$ depends linearly on the stage number n , and the increment $12\alpha_{C_t}$ gives the lattice specific-heat coefficient for the C_t layer. The α_{C_t} (mJ/mol K^4) thus obtained are 0.026 ± 0.001 , 0.025 ± 0.003 , and 0.033 ± 0.003 for potassium, rubidium, and cesium compounds, respectively. Since these values are almost the same as the value of $\alpha_C (=0.026 \pm 0.001 \text{ mJ/mol K}^4)$ for pure graphite,³ the C_t layers may be regarded as carbon layers in pure graphite. As seen from Fig. 4, ex-

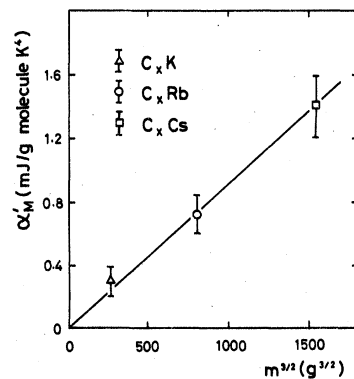


FIG. 5. The values of α'_M , derived from the intercepts of the straight lines in Fig. 4, are plotted as a function of $m^{3/2}$. The value of m refers to the atomic weight of the alkali-metal-atom species concerned.

trapolation of the line connecting data points for a given alkali metal-graphite combination to $n=0$ gives a hypothetical coefficient α'_M . As demonstrated in Fig. 5, α'_M is proportional to $m^{3/2}$, where m is the atomic weight of M . All these findings lead us to conclude that the acoustic modes inherent to the C_i layers coexist with those inherent to the C_b - M - C_b composite layers in compounds with stage numbers greater than 3.

On the other hand, the lattice specific heats of the first-stage compounds exhibit quite different behaviors depending on the intercalation species. In fact, the Debye temperatures of $C_8\text{Rb}$ and $C_8\text{Cs}$ are higher than those of the corresponding higher-stage compounds, whereas the Debye temperature of $C_8\text{K}$ is lower than those of higher-stage $C_x\text{K}$ compounds. No simple model applicable to the higher-stage alkali compounds is useful for first-stage compounds since these latter contain the most closely packed alkali metal atoms in each carbon layer and are more or less three dimensional in nature.

C. Additional specific heats

We reported previously that the specific-heat anomaly found for $C_x\text{Cs}$ arises from an optical-phonon mode related to the cesium atoms whose eigenfrequency is low enough to make a sizable contribution to the low-temperature specific heats. In the present experiment, a similar anomaly was found in the low-temperature specific heats of $C_x\text{Rb}$ as described in Sec. III.

For first-stage compounds, Horie *et al.* have calculated the dispersion relations of the phonon modes and predicted the existence of a *dispersionless* optical mode in the low-frequency region.¹⁷ The dispersionless mode should result in a large peak at a given frequency in the density-of-states curve of the phonon. The frequencies of the peaks are calculated to be 101 cm^{-1} ($\Delta = 145\text{ K}$) for $C_8\text{K}$ and 76 cm^{-1} ($\Delta = 109\text{ K}$) for $C_8\text{Rb}$. The calculated value for $C_8\text{Rb}$ is comparable to that reported here ($\Delta = 71\text{ K}$). Because the atomic weight of cesium is larger than that of rubidium, the Δ value for $C_8\text{Cs}$ is less than that for $C_8\text{Rb}$. A harmonic oscillator-type lattice vibration gives the famous Einstein specific heat, of which the low-temperature expansion can be expressed as

$$\Delta C = N_A k_B A (\Delta/T)^2 \exp(-\Delta/T), \quad (5)$$

where N_A is the Avogadro number, k_B is the Boltzmann constant, Δ is the so-called Einstein temperature, and A is a parameter whose physical meaning is discussed below. In comparison with Eq. (2), it is concluded that the specific-heat anomaly found for $C_x\text{Rb}$ is of the Einstein type and origin-

ates from a dispersionless optical mode the eigenfrequency of which occurs in a low-frequency region. The resulting parameters Δ and A are listed in Table I. In particular, the metal-concentration dependence of coefficient A for $C_x\text{Rb}$ and $C_x\text{Cs}$ is shown in Fig. 6.

In the case of higher-stage compounds, it was found that (1) the value of Δ depends not on the stage but on the intercalant species and (2) coefficient A is proportional to the alkali-metal-atom concentration. This behavior indicates that the anomalies found in higher-stage compounds are associated with the lattice vibrations of the C_b - M - C_b composite layers and, hence, are independent of the presence of the C_i layers. In the Einstein model, coefficient A is

$$A = (N/N_A)f,$$

where N is the total number of alkali metal atoms and f represents the degree of freedom of each alkali metal atom contributing to the Einstein specific heat. The fact that the A coefficients for higher-stage compounds fall along a straight line indicates that the f value is constant independent of the stage. The values are found to be 1.9 and 1.6 for $C_x\text{Rb}$ and $C_x\text{Cs}$ compounds, respectively. This suggests that the vibrational modes responsible for the Einstein specific heats are two-dimensional in

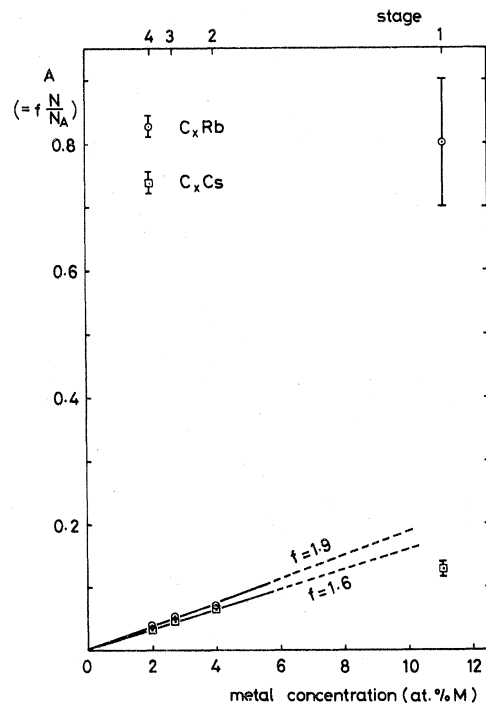


FIG. 6. The A coefficient in Eq. (5) is plotted against the concentration of rubidium or cesium atoms. The slopes of the straight lines indicate the values of f .

nature because f must be 3 when each alkali metal atom oscillates three-dimensionally at the Einstein frequency, $\omega_E = k_B \Delta / \hbar$. Therefore, the present results strongly suggest that these optical modes should be vibrations in the plane of the alkali metal atoms. The f value for C_8Cs is found to be 1.1, which is slightly lower than those for the corresponding higher-stage compounds. Campbell *et al.* have shown from the ^{133}Cs Mössbauer measurements on C_8Cs that the Cs atoms in the intercalated layers can vibrate freely within the plane perpendicular to the c axis but are hindered along the c axis because of the barrier produced by the carbon layers.¹⁸

In the case of C_8Rb , the value of f (≈ 7) is too large even if all vibrational modes associated with Rb atoms participate in the anomaly. According to Horie *et al.*,¹⁷ optical modes B_{2u} and B_{3u} associated with the carbon layers in C_8Rb are reported to have eigenfrequencies similar to those of the optical modes, which are believed to give rise to the anomaly. The fortuitous superposition of the B_{2u} and B_{3u} modes may result in an increase in the value of f .

The ratio Δ_1/Δ_n for both C_xRb and C_xCs was found to be approximately $\sqrt{2}$, where Δ_1 and Δ_n refer to the Einstein temperatures for the first- and higher-stage compounds, respectively. The $\sqrt{2}$ ratio may reflect the difference in the density of alkali metal atoms in the metal layer, i.e., the number of the nearest-neighbor atoms in the metal layers of

first-stage compounds is twice as great as that of the higher-stage alkali metal compounds.

The Einstein temperature, 145 K, for C_8K calculated by Horie *et al.*¹⁷ is probably too high to produce a noticeable contribution to the low-temperature specific heats over the temperature range studied. This contribution is expected to become measurable only at temperatures above 20 K.

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