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Low-temperature specific heats of graphite intercalation compounds with potassium and cesium

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Low-temperature specific-heat measurements in the temperature range between 1.5 and 5 K are reported for graphite intercalation compounds with potassium and cesium as follows: C_8K, $C_{24}K$, $C_{36}K$; C_8Cs, $C_{24}Cs$, $C_{36}Cs$, and $C_{48}Cs$. With increasing the alkali-metal concentration, the electronic-specific-heat coefficient γ increases for both the C_xK and C_xCs compounds, showing the lack of dependence on the solute species such as K or Cs. For the graphite-rich stage compounds ($x \geq 24$), the γ value can be reasonably well approximated in terms of the rigid-band model based on pure graphite. In C_8K and C_8Cs compounds, however, the rigid-band approach breaks down and the presence of the alkali-metal sheets, withholding an appreciable amount of conduction electrons, should be taken into account. A Schottky-type anomalous specific heat was observed in all compounds with cesium, but it was not obvious in compounds with potassium.

I. INTRODUCTION

The structure of graphite may be represented by a two-dimensional hexagonal network of atoms of interatomic distance of 1.42 Å, stacked in the order *AB AB* and separated by a distance of 3.35 Å, as shown in Fig. 1. The unit cells contain four atoms per cell and the atomic volume is 8.72×10^{-24} cm^{-3}. It is well recognized that the bonding related to the s, p_x, and p_y electrons in the hexagonal network is much stronger than the interplanar bonding which results from the π-orbital motion of p_z electrons, perpendicular to the network planes. Therefore, in the "lamellar"-type compounds, such as the alkali-graphite intercalation compounds, the alkali-metal atoms are easily accommodated in the layers between graphite layers by expanding the interlayer distance.[1] For a given alkali metal M, the resulting crystal compounds are known to form in several stages with the formulas C_8M, $C_{24}M$, $C_{36}M$, $C_{48}M$, and $C_{60}M$. All such stage compounds have been obtained with potassium, rubidium, and cesium, but lithium and sodium compounds appear to be difficult to form.[1] Very recently, the lithium compound C_6Li has been successfully prepared by Guerard and Herold,[2] and its specific heat measured in the liquid-He temperature range by Delhaes *et al.*[3] The crystal structure of the intercalation compounds has been studied by a number of authors.[4-6] The sequence of the layers is illustrated in Fig. 1 for the various compounds. As may be expected for a layer structure, the electrical conductivity shows a strong anisotropy in the directions parallel, or perpendicular, to the c axis.[1,7] Furthermore, an intercalation compound may be expected to show some special physical or chemical properties, possessed neither by the graphite nor by the intercalate substance. For example, superconductivity has been observed in C_8M compounds (M = K, Rb, and Cs) in the temperature range 0.02–0.55 K, but not in $C_{24}K$ down to 0.011 K.[8] The existence of superconductivity has been discussed in relation to the dimensionality of these compounds.[9] Recently Kondow and co-workers,[10,11] discovered molecular-sieve-type sorption on the $C_{24}M$ compounds (M = K, Rb, and Cs) at temperatures in the range of 77 K. These findings have attracted additional attention to the various intercalation compounds, pointing the need for a better understanding of their electronic structure. We report here low-temperature specific-heat measurements in a number of intercalation compounds with potassium and cesium, in the temperature range 1.5–5 K. The results are discussed in terms of the electronic and lattice properties of these compounds. A Schottky-type anomalous specific heat was observed in all compounds with cesium, but it was not obvious in compounds with potassium.

II. EXPERIMENTAL DETAILS

National spectroscopic graphite powder, SP-1, was used as supplied by the National Carbon Co., division of Union Carbide Corp. Total impurity content was guaranteed to be less than 6 ppm, and

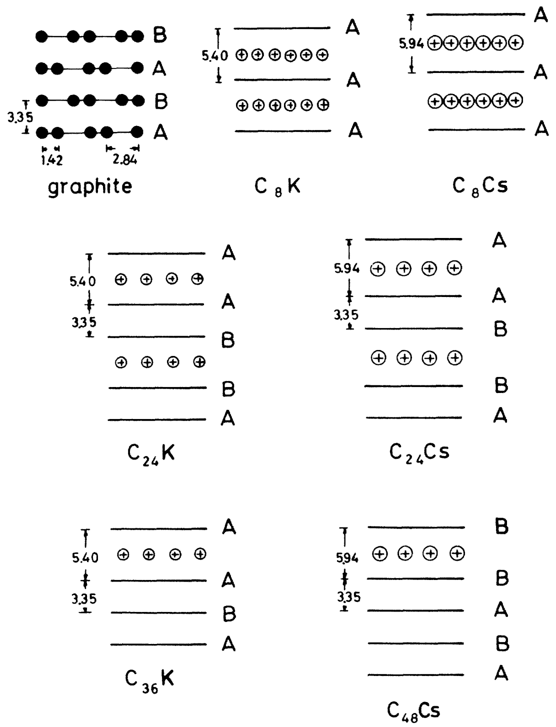

FIG. 1. Stacking sequences in graphite-potassium and graphite-cesium intercalation compounds. Each alkali-metal sheet is marked by ⊕ while the graphite layer is shown by the heavy line. The stacking layers of pure graphite are also shown. The interatomic and interlayer distances are shown in units of angstroms.

the powder had been graphitized at about 3000 °C. Average particle size was of the order of 10 μm.

The graphite-alkali-metal stage compounds were synthesized in a dual furnace (E) as shown in Fig. 2. The glass assembly shown in the figure was evacuated to a pressure of 10^{-5} Torr and the graphite powder in part A was heated at a temperature of 450 °C for several hours. The alkali metal placed in part B was distilled into parts C and D following which the necks b and c were sealed off. The resulting double-headed vessel was set in the dual furnace illustrated in Fig. 2 with the parts A and D heated at different temperatures T_1 and T_2, respectively. The temperatures T_1 and T_2 were controlled independently so that the first- or the second-stage compounds (C_8M and $C_{24}M$, respectively) could be prepared as required. The suitable combinations of temperatures T_1 and T_2 necessary for the preparation of a particular compound have been described elsewhere.[11] The formation of the intended compounds was initially confirmed by the color change and later the structure was verified by x-ray diffraction. The dual furnace method was mainly applied to the synthesis of the first- and second-stage compounds. Preparation of the higher-stage compounds by the dual-temperature method requires a very accurate temperature control and hence, for the present investigation, it was more convenient to produce the third- and fourth-stage compounds by "diluting" the C_8M compounds with a necessary amount of graphite. Each synthesized compound was sealed under vacuum in a Pyrex glass tube and annealed at 300 °C for about 3 d. During annealing, each tube was vigorously shaken at least twice a day, to ensure a well-homogenized sample. After homogenization, the samples were transferred and compacted into separate Au-plated copper containers fitted with Teflon-sealed lids suitable for low-temperature calorimetry. Metallic containers of this kind ensured a quick thermal response during subsequent measurements, and served to protect each sample from exposure to air and oxidation. The transfer from glass tubes to Cu containers was accomplished in a well-controlled dry box circulated with pure-argon gas. The transfer was done at the Westinghouse Research Lab., in Pittsburgh, Pa. (see Acknowledgments). The impurity level of H_2O and O_2 in the dry box was less than 1 ppm by volume. Argon was employed instead of helium, because it is immobile at liquid-helium temperatures and its presence in the container does not affect the measurements. Its possible contribution to the total heat capacity is negligible. According to Watanabe *et al.*[11], C_8M compounds (M = K, Rb, and Cs) are nonsorptive to argon. However, it appears that $C_{24}Cs$ can be sorptive, but not the $C_{24}K$. No information is available for higher-stage alkali-poor compounds. Thus, at least in the case of the $C_{24}Cs$, the presence of argon could affect the electronic structure or the lattice properties. However, this effect is not likely to be important and was not investigated.

The total weight of the sample was usually about 6–7 g, as listed in Table I. The gold-plated containers were about 18 g in weight, 45 mm in depth

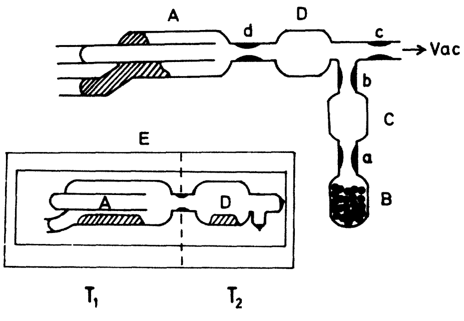

FIG. 2. Apparatus and dual furnace used for the preparation of the graphite–alkali-metal compounds.

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

Sample	Molar weight (g)	Weight (g)	γ (mJ/mol K^2)	α (mJ/mol K^4)	Θ_D (K)	δ (mJ/mol K^6)
C_8K	15.0211	5.9818	0.697 ± 0.006	0.1502 ± 0.0013	234.8 ± 0.7	0.001 35 ± 0.000 07
$C_{24}K$	13.0946	5.0287	0.241 ± 0.003	0.0375 ± 0.0007	372.9 ± 2.1	−0.000 35 ± 0.000 03
$C_{36}K$	12.7432	5.9537	0.189 ± 0.003	0.0339 ± 0.0007	385.2 ± 2.5	−0.000 33 ± 0.000 03
C_8Cs	25.4436	7.4161	0.63	0.049	341	
$C_{24}Cs$	16.8468	6.6177	0.25	0.085	284	
$C_{36}Cs$	15.2784	6.6815	0.19	0.072	300	
$C_{48}Cs$	14.4782	6.2453	0.16	0.060	319	
Graphite	12.011	6.2842	0.03 ± 0.01	0.026 ± 0.001	421 ± 4	−0.0002 ± 0.0001

and 10 mm i.d.. Their heat capacities were determined in separate experiments. The nominal composition of each sample, and the absence of oxidation, was confirmed by x-ray analysis.

Specific-heat measurements were made in a semiautomated differential calorimeter described previously.[12] The method allows an accurate measurement of heat capacities of two samples in the temperature range between 1.5 and ~5 K. Well-calibrated germanium resistors are used as thermometers. The thermal response to each heat input was sufficiently rapid, even for the alkali-poorest stages corresponding to the formula $C_{48}M$. Each experiment involved three runs yielding more than 100 data points between 1.5 and ~5 K.

III. EXPERIMENTAL RESULTS

The low-temperature specific heats C, for the C_xK and C_xCs compounds are plotted in Figs. 3 and 4 in the usual form of C/T vs T^2 in the liquid-helium temperature range. A molar quantity may be defined in the present analysis by the relation $(xA_C + A_M)/(1+x)$ for the C_xM compound, where A_C and A_M are the atomic weights of carbon and alkali metal, respectively. In the C_xK system, the deviation of the data for each compound from a straight line in the C/T vs T^2 plot is fairly small, indicating that the customary fitting equation $C = \gamma T + \alpha T^3 + \delta T^5$ can be employed. The electronic-specific-heat coefficient γ, the lattice-specific-heat coefficient α, the related Debye temperature Θ_D, and the deviation from the Debye model δ were calculated, using the data in the temperature range 1.5–4.2 K, and are summarized in Table I. On the other hand, in the C_xCs system, an unusually large deviation from a possible straight-line plot of the data was observed for all stage compounds studied. In the case of the C_8Cs compound, this deviation becomes clearly evident only at the temperatures above approximately 3 K. The temperature at which the deviation occurs, becomes lowered as the alkali-metal content decreases in higher stages. Assuming a linear trend below the temperature at which a deviation becomes obvious, a reasonable estimate can be made of the electronic-specific-heat coefficient γ, as well as the Debye temperature Θ_D, for the Cs-bearing compounds, by extrapolating each trend to 0 K. The deviation from a straight line is assumed to result from an additional contribution to the specific heat. The details of this interpretation are discussed in Sec. IV.

The low-temperature specific heat of pure graphite was also measured and the results are included in Figs. 3 and 4 for comparison. The graphite powder, identical to the material used for the intercalation compounds, was tightly compacted into

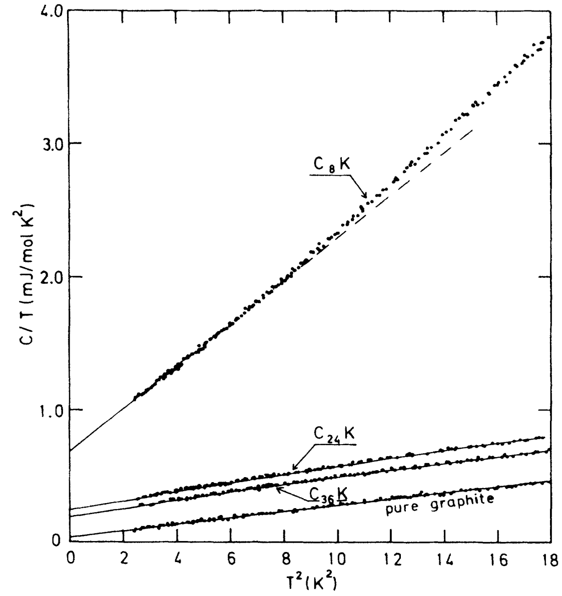

FIG. 3. Plots of C/T vs T^2, for the graphite-potassium intercalation compounds, as well as pure graphite, in the temperature range 1.5–4.2 K. Although the experiments were extended up to 6–7 K, no anomalous specific heat was observed for all compounds with potassium.

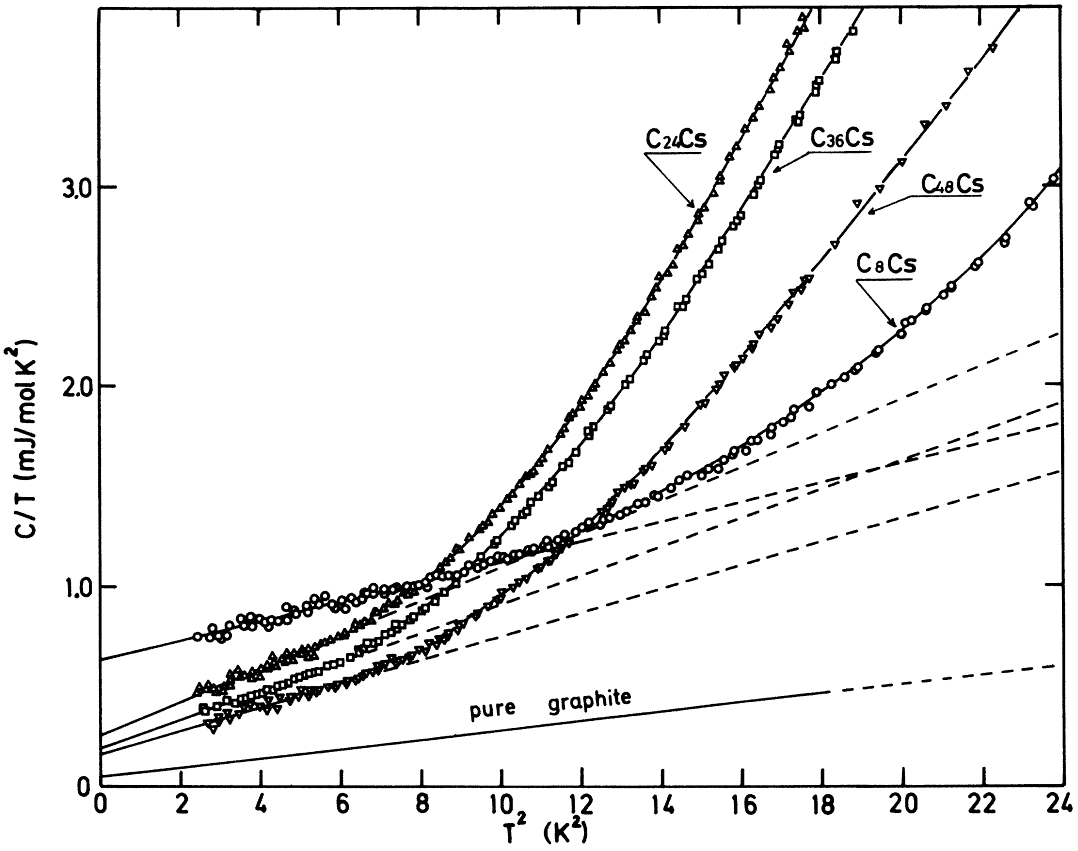

FIG. 4. Plots of C/T vs T^2, for the graphite-cesium intercalation compounds in the temperature range 1.5–5 K.

a cylindrical form (23 mm in height and 13 mm in diameter). The measurement was made without a container. The results showed no unusual features, such as may be expected if the graphitization was poorly done.[13]

IV. DISCUSSION

A. Electronic specific heat

The electronic-specific-heat coefficients (γ) for both the C_xK and C_xCs compounds are plotted in Fig. 5 as a function of alkali-metal concentration. The results indicate a nearly linear relationship for the graphite-rich stages. It can be also seen that the experimental γ values are almost independent of the solute species such as K or Cs. Thus, we expect the electronic structure of these compounds to be mainly determined by the effect of the distribution of the alkali-metal valence electrons over the graphite layers. Both C_8K and C_8Cs compounds have been reported to be superconducting, and the transition temperature T_c can be used to assess the electron-phonon enhancement factor λ utilizing McMillan's formula[14] $\lambda = [1.04 + \mu^*$

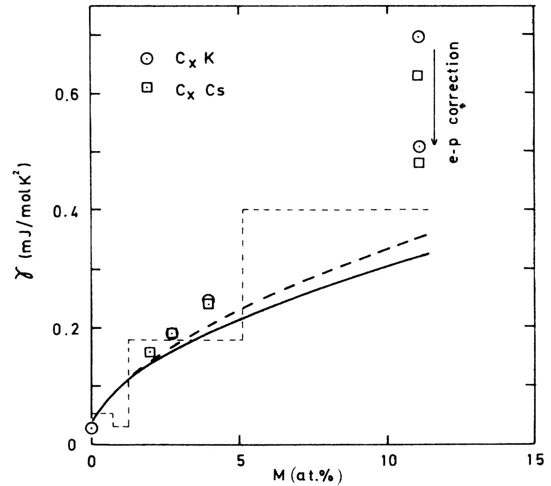

FIG. 5. Trend of the electronic specific-heat coefficient γ as a function of atomic percent of alkali metal. The dashed curve (----), was obtained by inserting the McClure's SW parameters and the value $1/x$ for n in Eq. (3). The full curve (——) includes a correction for the number of graphite atoms present in a mole of the C_xM compound, as discussed in the text. The thin dashed histogrammic curve (---) was reproduced from Willis *et al.* (Ref. 20).

$\times \ln(\Theta_D/1.45\ T_c)]/[(1-0.62\mu^*)\ln(\Theta_D/1.45\ T_c) -1.04]$, where the Coulomb repulsive constant μ^* is assumed to be 0.1. Taking T_c values as 0.55 and 0.135 for C_8K and C_8Cs, and the Debye temperatures from Table I, the resulting λ values are 0.37 and 0.30, respectively. The corrected γ values, using the relationship $\gamma_{\text{cor}} = \gamma_{\text{exp}}/(1+\lambda)$, become 0.51 and 0.48 mJ/mol K^2 for C_8K and C_8Cs, respectively.

Recently, Carver[15] studied the NMR spectra of ^{13}C and ^{133}Cs nuclei in powdered samples of the C_xCs compounds ($x=8$, 24, 36, 48, and 60) at temperatures between 1.3 and 4.2 K. The Knight shift for ^{133}Cs is 0.29% in C_8Cs and zero in both $C_{24}Cs$ and $C_{36}Cs$, within the accuracy of ±0.02%. These results imply that there remains some electronic charge density at the cesium nuclear sites in C_8Cs, but only a negligible amount in $C_{24}Cs$ and $C_{36}Cs$, being probably further reduced in higher Cs-poor stages. Carver estimated the degree of ionization in C_8Cs to be only 0.55, as compared with the Knight shift in the metallic cesium, and to be complete in the Cs-poor stages. The lack of solute-species dependence in the measured γ values suggests more or less the same degree of ionization occurring in the corresponding C_xK compounds. These findings are a useful guide for the discussion of the corresponding electronic states. The $C_{24}M$ (M = K, Rb, and Cs) compounds undergo a reversible transformation from a disordered to an ordered state at −175, −114, and −110 °C, respectively.[16,17] This involves a redistribution of alkali-metal atoms in the metal layers. In the present analysis, we will not consider this effect.

In the case of the alkali-poorer stages, where the alkali-metal layers are completely ionized, valence electrons of alkali metals may be assumed to be evenly distributed over all graphite layers. This model approximates the rigid-band model of pure graphite, with the alkali-metal electrons filling the density-of-states band of pure graphite. McClure[18] calculated the density of states for pure graphite based on the Slonczewski and Weiss (SW) model. It was found that, at least in the energy range within 0.4 eV above the Fermi level of pure graphite, the density-of-states curve can be well approximated by a linear equation

$$N(E) = (2/\sqrt{3}\,\pi\gamma_0^2)\,[E - \tfrac{1}{2}(\Delta+\gamma_2)], \tag{1}$$

where the SW parameters γ_0, γ_2, and Δ were chosen by McClure as 2, 0.017, and 0.018 eV, respectively. Williamson *et al.*[19] proposed a different set of the SW parameters to account for their de Haas–van Alphen data. Willis *et al.*[20] recently calculated by means of the variational method the histogrammic density-of-states curve for pure graphite over a wide energy range extending more than 80 eV from the bottom of the band. The resulting density of states may be well approximated by a straight line within 2 eV of the Fermi level, although the resolution is rather poor because of the choice of a relatively wide width for each histogram (ΔE = 0.5 eV). As far as the density-of-states curve is concerned, the result obtained by McClure agrees better with that by Willis *et al.*, than that by Williamson *et al.* Furthermore, his density-of-states curve fits well to the present results in the dilute range. Thus, McClure's band structure will be referred to as that of pure graphite.

The density-of-states value at the Fermi level, or the γ value, can be easily obtained from Eq. (1) as a function of the number of added electrons n per graphite atom:

$$\gamma = 2.357(\pi\gamma_0^2\sqrt{3})^{-1} \times[(\Delta+\gamma_2)^2 + 4\sqrt{3}\,\pi\gamma_0^2 n]^{1/2}(\text{mJ/mol K}^2), \tag{2}$$

where Δ, γ_0, and γ_2 are the SW parameters in the units of electron volts.

The γ values, obtained by inserting McClure's SW parameters into Eq. (2), are plotted in Fig. 5 as a dashed curve. According to the present definition of a molar quantity, the number of electrons donated by the alkali-metal atoms to a mole of the C_xM compound will be given by $N_A/(1+x)$, if each alkali atom contributes one valence electron to the graphite band, and N_A is the Avogadro number. All these electrons are assumed to distribute evenly over the $N_Ax/(1+x)$ carbon atoms. Thus, the number of electrons n per graphite atom is denoted by the relation $n = [N_A/(1+x)]/[N_Ax/(1+x)] = 1/x$ for the C_xM compound. For the sake of convenience, this relation is used also for the C_8M compounds. Strictly speaking, less than one valence electron per alkali atom will be contributed to the graphite band in these compounds, because of incomplete ionization. It should be noted that the calculated γ value always refers to 1 mol of graphite atoms, i.e., N_A number of carbon atoms, whereas the experimental γ value represents the behavior of $N_Ax/(1+x)$ carbon atoms and $N_A/(1+x)$ alkali atoms. As far as the γ value is concerned, a completely ionized alkali-metal layer in an alkali-poor stage compound may be ignored. If this is done, then the rigid-band γ value should refer to the effective number of carbon atoms in a molar compound. The corrected rigid-band curve indicated by the solid curve in Fig. 5 agrees fairly well with the corresponding experimental values for all alkali-poorer stages (x = 24, 36, 48, and probably 60). This implies that the ionized metal sheets produce essentially no contribution to the electronic specific heat, and that the electronic structure of these compounds can be reasonably well approximated in terms of the rigid-band model based on pure graphite.

In the C_8M compounds, the situation seems to be quite different, because no agreement is shown between the experimental and the calculated γ values, even though the electron-phonon interaction is taken into account. The agreement is further reduced, if the number of valence electrons n, per graphite atom is changed from $\frac{1}{8}$ to 0.55/8 to account for the incomplete ionization. It is quite clear that the contribution of alkali-metal sheets should not be ignored, because they still withhold an appreciable amount of conduction electrons. In such a circumstance, an independent treatment of both graphite and alkali-metal sheets will not be appropriate and, instead, the compound should be treated as a substance entirely different from its component metals. In fact, Inoshita *et al.*[21] recently calculated the band structure of the C_8K compound based on the tight-binding approximation. They found that dispersion relation in the vicinity of the Fermi level corresponding to the first-stage compound C_8K no longer resembles that of pure graphite, even though the characteristic features of graphite are retained in the lower-energy range. This indicates that the electronic structure near the Fermi level in a C_8M compound cannot be described in terms of any simple combination of the electronic features of the parent graphite and the alkali component. On the other hand, even in the case of the C_8K compound the density of states is expected to approach that of pure graphite, as the Fermi level is lowered towards the value corresponding to the alkali-poorer compounds. The effect of the alkali-metal sheets on the electronic structure will be further lessened in these compounds, as compared with the C_8K compound. Thus, the band structure near the Fermi level in the alkali-poorer compounds ($x \geq 24$) is likely to be well approximated by that of pure graphite. These features are quite consistent with the present interpretation of the behavior of the electronic specific heats in both the C_xK and C_xCs compounds. Accordingly, the presence or the absence of superconductivity in C_8M and $C_{24}M$ compounds should be argued from the point of view of the striking difference in their electronic structure.

B. Comparison with other physical properties

In Sec. IV A, it was argued that the presently measured γ values reflect the density of states at the Fermi level. Particularly, it was shown that the γ value for the stage compounds poor in alkali-metal content can be interpreted in terms of the rigid-band model based on pure graphite. It is significant to compare the present results with other physical properties related to the density of states at the Fermi level. Magnetic studies at room temperature, for a sequence of alkali-metal compounds C_xM (M = K and Rb), show that the marked diamagnetism of graphite ($\chi \approx -84 \times 10^{-6}$ emu/g-at) is destroyed even for the most dilute $C_{60}M$ compound, and that all such compounds exhibit weak paramagnetism.[1,4] The apparent disappearance of diamagnetism in graphite by the addition of a small amount of an alkali metal is not yet fully understood. The magnetic susceptibility in a nonmagnetic material may be considered to consist of three major contributions: the Pauli paramagnetism, the Landau diamagnetism, and the ionic diamagnetism due to the orbital motion of core electrons. If the ionic diamagnetism is properly subtracted, the remaining magnetic susceptibility is expected to be related to the density of states at the Fermi level. Hurd and Coodin[22] calculated the diamagnetic susceptibilities of various free ions from the well known formula of Stoner, using the atomic wave functions obtained by Herman and Skillman. The values for K^+ and Cs^+ ions are -14.33 and -38.66×10^{-6} emu/g-at., respectively. To account for the ionic contribution of the carbon atoms, all four valence electrons are assumed to be localized around each atom while the additional electrons donated by the metal atoms move freely within the carbon layers. Henry and Rogers[23] cite the value of susceptibility for the free C atoms to be -10.8×10^{-6} emu/g-at., which was deduced from the wave functions obtained by Jucys[24] with exchange interaction taken into account. This agrees with the value of -6.0×10^{-6} emu/g-at. estimated from Pascal's law.[25]

The ionic susceptibility in the C_xM compounds may be approximately estimated from the relation $\chi_C[x/(1+x)] + \chi_M[1/(1+x)]$, where χ_C and χ_M represent contributions from the carbon and the metal, respectively. The corrected susceptibility value is believed to represent the value for the conduction electrons, as shown in Fig. 6. It can be seen that this value initially increases and soon levels off, as the number of alkali-metal atoms increases.

In addition to the Knight shift, Carver[15] measured the spin-lattice relaxation time T_1 of the ^{13}C nuclei in the C-Cs compounds. The relaxation time T_1 is known to be inversely proportional to the square of the density of states at the Fermi level. In Fig. 6, the value of $\sqrt{1/T_1}$ is plotted as a function of Cs concentration. It can be seen again that the trend increases more or less linearly up to 4-at.% Cs, corresponding to the $C_{24}Cs$ compound, but the value for the C_8Cs compound is much lower than the linear extrapolation from lower concentrations. Thus, the composition dependence of χ_{cond} and T_1 is quite consistent with that of the γ values, leading a strong support to the possibility that, up to the

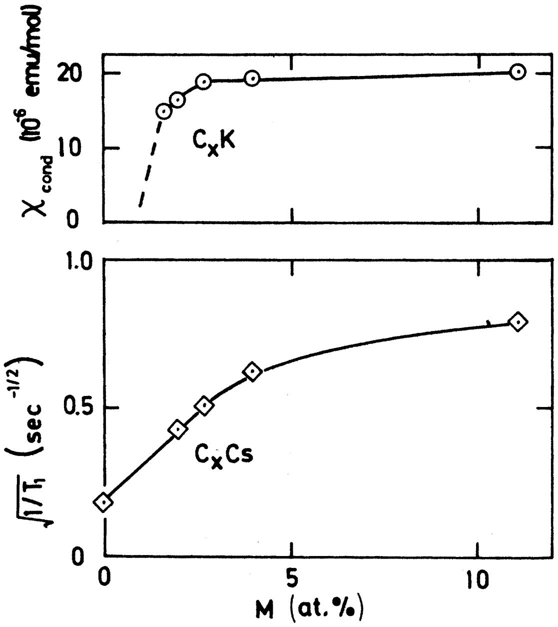

FIG. 6. Trend of the magnetic susceptibility due to conduction electrons in the graphite-potassium compounds (Ref. 4), and of the square root of the inverse T_1 temperature for the graphite-cesium compounds (Ref. 15). Both quantities are considered to be proportional to the density of states at the Fermi level.

composition of the $C_{24}M$ compound, the density of states at the Fermi level generally conforms to the rigid-band approximation based on the pure graphite. However, the three different properties in the C_8M compound indicate a different behavior when compared with the above carbon-rich compounds. The electronic structure of C_8M, particularly near the Fermi level, by no means approximates that of pure graphite.

C. Lattice specific heat

As described in Sec. III, the specific heat C in all C_xK compounds can be fitted very well to the usual equation $C = \gamma T + \alpha T^3 + \delta T^5$. As shown in Fig. 7, the Debye temperature Θ_D, related to the T^3 coefficient α, is found to decrease more or less linearly with increasing potassium concentration. The analysis for C-Cs compounds is less accurate, because of the presence of an additional specific-heat term ΔC. Here, the Debye temperature was roughly estimated by assuming the linear trend at the lower temperature range, as discussed in Sec. III. Thus, the T^5 coefficient δ was ignored. In contrast with the C-K compounds, the Θ_D value in Fig. 7 decreases more rapidly with addition of the Cs atoms, but the value for C_8Cs is exceptionally high, compared with the other three compounds, resulting in a minimum in the plotted Debye temperature trend. It is not clear whether or not the unusual behavior of the Debye temperature in the C-Cs compounds is associated with the presence of the additional specific heat ΔC, as discussed in Sec. IV D.

D. Schottky specific heat in C-Cs compounds

As can be seen in Fig. 4, an unusual deviation from linear relationships in the C/T vs T^2 plots was observed for all Cs compounds. Various attempts to fit the data to a power series expansion of the form $C = \sum_{n=1}^{9} a_n T^n$ (anticipating not only higher odd terms resulting from the deviation from the Debye model, but also a two-dimensional character with even power terms), were unsuccessful. Instead, we assume that the deviation from the possible straight line plots arises from an additional contribution to the specific heat. The additional specific heat ΔC may be, therefore, isolated from the total value by subtracting the "normal" part, which is derived from the equation $C = \gamma T + \alpha T^3$, with the coefficients γ and α as described in Sec. III. If ΔC arises from a Schottky-type phenomenon in a two-level system, it should obey the expression

$$\Delta C = N k_B (g_1/g_0) (\Delta/T)^2 e^{-\Delta/T} (T \ll \Delta) , \qquad (3a)$$

$$\Delta C = N k_B g_0 g_1 (g_0 + g_1)^{-2} (\Delta/T)^2 \quad (T >> \Delta), \qquad (3b)$$

where Δ is the energy-level separation in the scale of temperature, g_1 and g_0 are the degeneracies of the upper and lower levels, N is the number of "excitations" participating in this phenomenon, and k_B is the Boltzmann constant. Hence, if the characteristic temperature Δ exceeds the

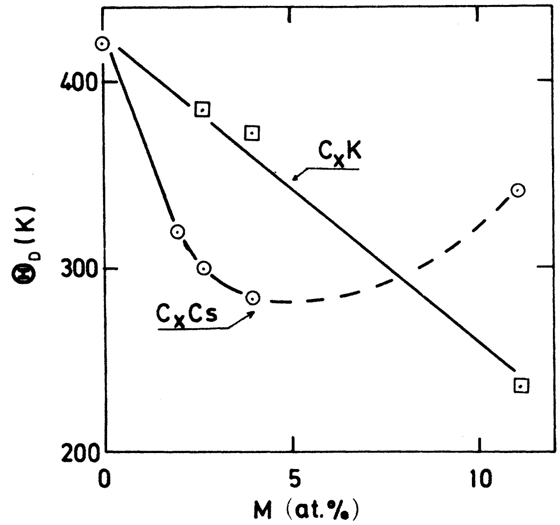

FIG. 7. Change in the Debye temperature Θ_D as a function of atomic percent of alkali metal, for both C_xK and C_xCs compounds.

liquid-He temperature range, the plot of $\ln[(\Delta C)T^2]$ vs $1/T$ should be linear, the parameters Δ and $N(g_1/g_0)$ being given by the slope and the intercept of the straight line, respectively. In fact, the data for all Cs compounds when plotted in this way are found to fall on a straight line, as typically shown in Fig. 8 for the $C_{36}Cs$ compound. The values of Δ and $N(g_1/g_0)$ are listed in Table II. It is seen from the table that the characteristic temperature Δ is about 48 K for C_8Cs and is almost constant near 34 K for the higher stages $C_{24}Cs$, $C_{36}Cs$, and $C_{48}Cs$. An estimate of the value of g_1/g_0 requires additional information concerning the value of N. The Cs atoms seem to play an important role in this phenomenon, since the value $N(g_1/g_0)$ increases more or less linearly with cesium concentration. Provided that each Cs atom is responsible for the Schottky effect, N may be taken as the number of Cs atoms per mole, i.e., $N_A/(x+1)$, for a C_xCs compound (N_A is Avogadro's number). With this assumption for N, the g_1/g_0 value can be uniquely determined and is found to be almost constant at 1.6, for the three compounds $C_{24}Cs$, $C_{36}Cs$, and $C_{48}Cs$, and about 1.1 for the compound C_8Cs. These results are listed in the last column of Table II. We conclude that a two-level Schottky specific heat is present in all C_xCs compounds, and that the level separation and the ratio of degeneracies of the upper and lower levels are almost identical in the alkali-metal poorer compounds ($x = 24$, 36, 48, and probably 60), while a slightly lower value is indicated for the C_8Cs compound.

Although it is clear that the presence of Cs atoms causes the Schottky effect, it is not possible from the present results to speculate what are the energy levels associated with this phenomenon. One possibility is the migration of the Cs atoms in the graphite layers. For example, a Schottky effect is typically observed in paramagnetic salts in which magnetic dipoles dispersed in the matrix can undergo a transition between levels independently of one another. This effect usually occurs at, or below, the liquid-He temperature range, leading to an ordinary energy separation between levels of the order of a few K. However, in the present case, the energy separation is approximately 40 K. Furthermore, it appears very unlikely that the proposed Schottky effect can be attributed to the same mechanism as that observed in the paramagnetic salts, because the densely packed nonmagnetic Cs atoms hardly resemble these substances. In order to throw more light on this problem, it would be of great interest to extend the temperature range of the specific-heat measurements to the temperature of liquid nitrogen, and also to measure the various other properties, particularly the magnetic susceptibility, in the same wide temperature range.

TABLE II. Schottky-type specific heats in C_xCs compounds. The errors are roughly estimated from a degree of uncertainty involved in subtracting "normal" specific heat from total specific heat (See Fig. 4).

Sample	Δ (K)	$(g_1/g_0)(N/N_A)$	N/N_A[a]	g_1/g_0
C_8Cs	47.6 ± 1.0	0.126	$\frac{1}{9}$	1.1 ± 0.1
$C_{24}Cs$	35.1 ± 1.0	0.0647	$\frac{1}{25}$	1.6 ± 0.1
$C_{36}Cs$	33.4 ± 1.0	0.0444	$\frac{1}{37}$	1.6 ± 0.1
$C_{48}Cs$	33.9 ± 1.0	0.0320	$\frac{1}{49}$	1.6 ± 0.1

[a] N/N_A for a compound C_xCs is given by $1/(1+x)$, where N_A is the Avogadro number.

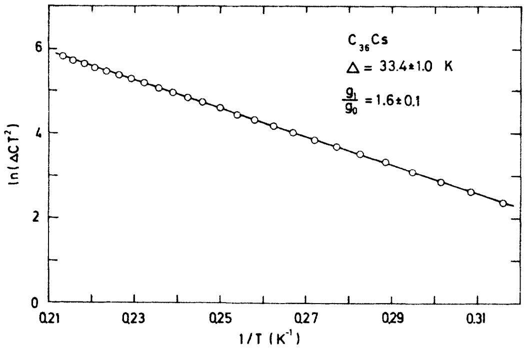

FIG. 8. Plot of an additional specific heat, in the form of $\ln(\Delta CT^2)$ vs $1/T$, for the $C_{36}Cs$ compound. The value ΔC is an additional specific heat due to the proposed "Schottky" effect. The parameters Δ and g_1/g_0 can be obtained from the slope and the intercept of the straight line, respectively. The data points marked by open circles do not necessarily correspond to actual measured values in Fig. 4, but may represent calculated values at different temperatures.

Note added in proof. At the Franco-American comerence on the graphite intercalation compounds at La Napoule, France (May 23–27, 1977), we proposed an alternative interpretation for the origin of the additional specific heat ΔC. Here, ΔC was attributed to the possible presence of the low-frequency optical mode associated with the motion of Cs atoms relative to the graphite planes and its contribution to the specific heat was approximated by the Einstein model. In the temperature range $T \ll \theta_E$, where θ_E is the Einstein temperature derived from the characteristic frequency ω_E of the optical mode ($h\omega_E = k_B\theta_E$), the Einstein formula is reduced to the similar form as Eq. (3a); the data analysis in the text remains valid even in this case and the parameter Δ in Table II should be read as the Einstein temperature θ_E. Hence, the frequences of the optical modes are 33 and 24 cm^{-1} for C_8Cs and the higher stages compounds, respectively. The presence of such a low-frequency lattice mode in these compounds was also proposed by M. S. Dresselhaus, G. Dresselhaus, and their associates in connection with their presentation on the Raman spectra of these intercalation compounds at the same meeting. Proceedings of this conference will appear in a special issue of Materials Science and Engineering.

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