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Electronic properties, resistive anomalies, and phase transitions in the graphite intercalation compounds with K, Rb, and Cs

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Overall resistivity-temperature data for the graphite intercalation compounds of potassium, rubidium, and cesium at stages 1 and 2, and of potassium at stages 3 and 4, at room temperature and below are presented. Except in the stage 1 compounds two resistivity anomalies are observed for each compound between 77 and 300 K. Correlation with known structural studies suggests the anomalies are due to interplanar and intraplanar ordering within the intercalant layers upon cooling and this conclusion is shown to be qualitatively consistent with the temperature dependence of the Hall coefficient and magnetoresistance of KC_{24} through the anomalies, which can be explained in terms of carrier mobility rather than carrier density changes. It is suggested that the details of the ordering process may be unique in each compound.

I. INTRODUCTION

The intercalation compounds of graphite with potassium, rubidium, and cesium constitute a group of lamellar compounds which typify the "donor" class of this group of materials, and which can readily and reproducibly be prepared and characterized. Several reviews of their electronic properties have recently appeared[1,2] and much additional research was described at the recent Franco-American Conference on the Intercalation Compounds of Graphite.[3]

Each of these compounds can be prepared in a series of stoichiometric "stages", each "stage" being defined by the number of intervening carbon layers between alkali-metal layers. Stage 1 compounds have the stoichiometric formula MC_8, the M atoms being considered as close-packed relative to the graphite layers, while higher stages (n) have the formula MC_{12n} with the alkali-metal layers then necessarily containing vacancy sites which may, or may not be in an ordered array.[4]

We report here extensive studies of the electronic properties of the stage 1 and stage 2 compounds KC_8, RbC_8, CsC_8, KC_{24}, RbC_{24}, and CsC_{24} and of KC_{36} and KC_{48}. The compounds selected for study include a sequence of stages for the potassium compounds and a transverse sequence through the metals at stages 1 and 2. Except for the stage 1 compounds we observed two resistive anomalies in each compound between 77 and 300 K and selected KC_{24}, in which these anomalies are only about 1 K wide, for more detailed study of the temperature dependence of the Hall effect and the magnetoresistance through the anomalies. The results are discussed in light of known structural studies[5-8] and of a recent magnetic susceptibility study of KC_{24}.[9]

Some of the resistive anomalies are at temperatures very close to structural phase transitions observed in the stage 2 compounds by Parry and coworkers and we attribute the anomalies to carrier mobility changes arising from such order-disorder transitions. The x-ray diffraction patterns for stage 2 compounds implied that the metal layers in KC_{24}, RbC_{24}, and CsC_{24} were disordered at room temperature, but at least partially ordered by 77 K with one phase transition per compound noted. The ordering was both intraplanar and interplanar at 77 K. Similar structural phase transitions were observed by Ubbelohde and coworkers in the "acceptor" intercalation compounds with nitric acid which showed anomalous electronic properties in the same temperature region as the structural transion.[10,11] More recent x-ray studies have shown two structural phase transitions in KC_{24} in good agreement with our resistive anomalies.[8] Similar phase changes may be a near universal feature of graphite intercalation compounds as pointed out in a recent review.[2]

II. EXPERIMENTAL TECHNIQUES

The samples were all created based on highly-oriented pyrolitic graphite (HOPG)[12] cut into the shape of a five-arm bridge by air-abrasion techniques. This cutting method minimizes internal damage which may occur with other cutting techniques.[13] All samples were 1 cm between potential measurement arms, ~0.2 cm wide and about 0.05 cm thick. Electrical connections were made by platinum wires and sintered gold contacts. The five wires were passed through a fine glass tube support structure which permitted stress-free expansion of the sample due both to intercalation and temperature changes. The entire structure was enclosed in a rectangular Pyrex envelope, the leads leaving through hand-fabricated platinum-glass seals. The rectangular Pyrex was then joined to a longer Pyrex reservoir into which the alkali-metal could be distilled. Following distillation and sealoff the samples were intercalated using the standard double-zone technique, the final "stage" being controlled by the temperature difference between the hot (graphite) zone and the cooler (metal) zone. Further details are given elsewhere.[14]

The samples were characterized by $(00l)$ x-ray studies using Mo-K_α radiation. The x-ray measurements were made throughout the intercalation process, which was spread over several days, allowing careful observation of the formation of successive stages. Chemical analysis of the samples was not possible, but reproducible agreement between several samples made by identical techniques and used in a wide variety of studies suggest that the stoichiometry is close to the stated formulas.

A constant current of between 10 and 100 mA was passed through the end-contacts of the samples, and the resistive voltage measured at the side arms was recorded as a function of temperature by a semiautomatic system. Data was taken during warming at rates not greater than 1 K/min and for high-resolution scans as low as 100 mK/min. For magnetoresistance studies fields up to 20 kOe were used. Hall voltages were obtained in similar fields using the central fifth arm, initially resistively balanced against the two potential arms. While qualitative studies of magnetoresistance against temperature could be obtained by comparing warm drifts in zero field and in a 15 kOe field the magnetoresistance of the thermometer prevented accurate quantitative analysis of such data. The quantitative magnetoresistance and Hall coefficients reported below were obtained by performing eight field sweeps at each constant temperature with successively reversed current and magnetic field.

III. RESULTS

A. Temperature dependence of electrical resistivity and resistive anomalies

The a-axis electrical conductivity (σ_a) of each of the materials studied is shown in Table I for the fixed temperatures 4.2, 77, and 300 K. In the potassium compounds the conductivity at 300 K continues to increase with stage, while at 77 K it reaches a maximum at stage 3 (KC_{36}). At 300 K the conductivity seems to be determined more by particular stage than by the species of alkali metal, but comparison of the three stage 2 compounds at 77 K shows greater dependence on the individual alkali metal, possibly because of differing natures of the ordered states at

TABLE I. Summary of dc conductivity along a axis σ_a in $\Omega^{-1}\,\mathrm{cm}^{-1}$.

Material		Temperature	
	300 K	77 K	4.2 K
KC_8	1.1×10^5	1.0×10^6	2.4×10^7
KC_{24}	1.7×10^5	1.1×10^6	4×10^6
KC_{36}	2.1×10^5	1.15×10^6	4.2×10^6
KC_{48}	2.2×10^5	8.7×10^5	2.6×10^6
RbC_8[a]	1.0×10^5	8.6×10^5	1.2×10^7
RbC_{24}	1.5×10^5	5.8×10^5	...
CsC_8[a]	1.0×10^5	7.9×10^5	...
CsC_{24}	1.7×10^5	8.0×10^5	3.0×10^6
CsC_{36}[a]	1.2×10^5	4.6×10^5	9.5×10^5
Graphite	2.5×10^4	3.8×10^4	...

[a]From Ref. 16.

TABLE II. Summary of observed resistivity anomalies and known structural transitions. T_L and T_U are the upper and lower anomaly temperatures, corresponding to the high-temperature end of each resistive anomaly. The ΔT's are the anomaly widths. The f's are the fractional change in ρ at each transition. T_M gives the temperatures of observed structural changes.

Material	T_L (K)	ΔT_L (K)	f_L	T_U (K)	ΔT_U (K)	f_U	T_M
$C_{24}K$	95	0.5	0.07	123	1	0.08	98 ± 3[a] 95, 123[b]
$C_{36}K$	95	13	0.1	~250	~20	~0.05	. . .
$C_{48}K$	92	12	0.12	250	20	0.1	. . .
$C_{24}Rb$	106	16	0.1	172	14	0.05	159[c]
$C_{24}Cs$	180	14	0.09	230	10	0.03	163[c]

[a] Ref. 5. [b] Ref. 18. [c] Ref. 7.

77 K. Data at 4.2 K is only partially complete due to difficulties with thermal emf which will be overcome by planned ac measurements.

While Table I shows the overall trend of the electrical conductivities, our present major concern is with the resistive anomalies discovered in the temperature range 77 to 300 K and the temperature dependence of the electrical resistivity ($\rho_a = 1/\sigma_a$) near these anomalies which are summarized in Table II. We discuss the compounds in turn below:

(i) *Stage* 1 *compounds*: KC_8, RbC_8, and CsC_8. No sharp anomalies were observed in the resistivity (ρ_a) of the stage 1 compounds KC_8, RbC_8, and CsC_8. The temperature dependence of ρ_a was stronger than linear with temperature, but the presence of thermal emf particularly below 77 K made accurate analysis difficult. An ac resistivity study of ρ_a vs T is presently in progress for these compounds. The absence of resistivity anomalies is consistent with the x-ray observations which show that the intercalated metal layers are fully ordered at room temperature.[5-7] Recent neutron scattering data shows that structural reordering occurs only at high temperature, though the effect of such reordering on the electrical resistivity is not yet known.[15]

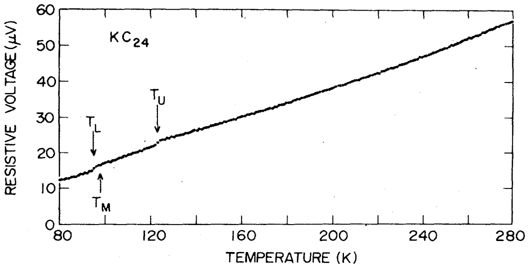

FIG. 1. Resistive voltage at constant current for KC_{24} between 80 and 280 K. The anomalies are marked at T_L and T_U but are more clearly seen in Fig. 6. The previously known order-disorder transition is at T_M (Ref. 5), but one close to T_U has recently been observed (Ref. 18).

(ii) *Stage* 2 *potassium graphite*: KC_{24}. The resistive voltage across a sample of KC_{24} between 80 and 300 K is shown in Fig. 1. The resistive anomalies at T_L (95 K) and T_U (123 K) are apparent as 8% and 7% step increases in the resistivity with increasing temperature. The anomaly at T_L is only 0.5 K wide, while that at T_U is 1 K wide. Plots of $d\rho_a/dT$ show λ-like anomalies at both T_L and T_U[16] though this does not *necessarily* imply, based on existing experimental data, that they are second-order transitions. The data in Fig. 1 was taken on a digital system with limited resolution, but analog sweeps through the two anomalies show that whereas the one at T_L terminates in a sharp break at its upper end, the one at T_U has a more rounded form. The anomalies are summarized in Table II.

Between T_L and T_U the resistivity is linear in the temperature with a slope of $2.5 \times 10^{-2}\ \mu\Omega\,\mathrm{cm\,K^{-1}}$. The temperature dependence of the resistivity for $125 > T > 300$ K can best be analyzed in terms of a linear increase of about $2 \times 10^{-2}\ \mu\Omega\,\mathrm{cm\,K^{-1}}$ with an added exponential contribution with an activation energy of about 750 K. This analysis provides a lower standard deviation than a linear term plus any other simple power of T. The linear term is typical of a metal at high temperatures, while the exponential contribution above T_U suggests a resistive process associated with an activation energy of about 0.066 eV arising from a mechanism which develops upon warming through T_U.

Between 4.2 and 80 K the temperature dependence of the resistivity cannot be characterized well from present dc data due to the presence of thermal emf; ac measurements are in progress. However, it appears that close to 4.2 K the resistivity varies approxi-

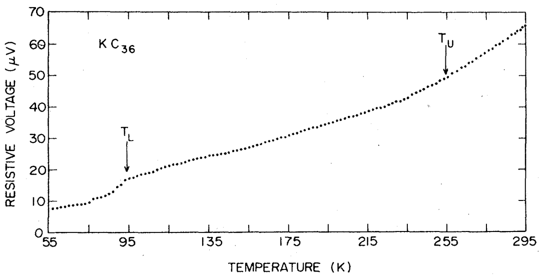

FIG. 2. Resistive voltage at constant current for KC_{36} between 55 and 275 K. The anomalies are marked at T_L and T_U, though the exact assignment of T_U is difficult (see text).

mately as T^3 plus a constant contribution and tends towards a linear dependence before T_L is reached, with $d\rho_a/dT$ near T_L very close to the value between T_L and T_U.

(iii) *Stage* 3 *potassium graphite*: KC_{36}. The temperature dependence of the resistive voltage for a sample of KC_{36} is shown in Fig. 2. Again two major anomalies are apparent, one being a broad step, about 10 K wide ending at 95 K. From 95 to about 230 K the resistivity is linear in temperature, with a slope of 1.38×10^{-2} $\mu\Omega\,\mathrm{cm\,K^{-1}}$. Between 230 and 250 K a second anomaly occurs, consisting of a region almost 20 K wide where $d\rho_a/dT$ increases very rapidly reaching, by 250 K, a value of 3×10^{-2} $\mu\Omega\,\mathrm{cm\,K^{-1}}$. The temperature dependence of $d\rho_a/dT$ above 250 K can again be described by a linear term and an exponential component, but the limited temperature range available prevents accurate quantitative analysis with present data. The anomalies are summarized in Table II.

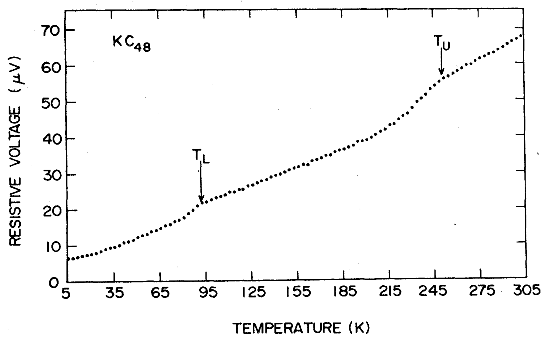

FIG. 3. Resistive voltage at constant current for KC_{48} between 5 and 305 K. The anomalies are marked at T_L and T_U.

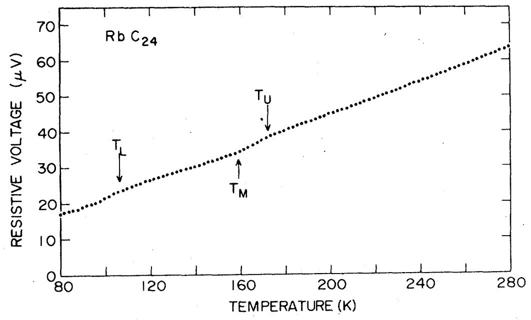

FIG. 4. Resistive voltage at constant current for RbC_{24} between 80 and 280 K. The anomalies are marked at T_U and T_L and the known order-disorder transitions are marked at T_M.

(iv) *Stage* 4 *potassium graphite*: KC_{48}. The temperature dependence of the resistive voltage for a sample of KC_{48} is shown in Fig. 3 for the temperature range 5 to 305 K. Two resistive anomalies are again apparent, broad as in KC_{36} rather than narrow as in KC_{24}. One stretches from about 80 to 95 K with a second from 230 to about 250 K. Both reflect increases of about 10% in the resistivity. The temperature dependence below T_L changes from approximately T^3 plus a constant close to 5 K, to linear between 50 and 80 K. The presence of thermal emf at the lowest temperatures is less serious in this more resistive sample. Between T_L and T_U the temperature dependence is again linear with a slope of 1.3×10^{-2} $\mu\Omega\,\mathrm{cm\,K^{-1}}$. Above T_U the accessible temperature range was not enough to characterize the temperature dependence, but the initial slope $d\rho_a/dT$

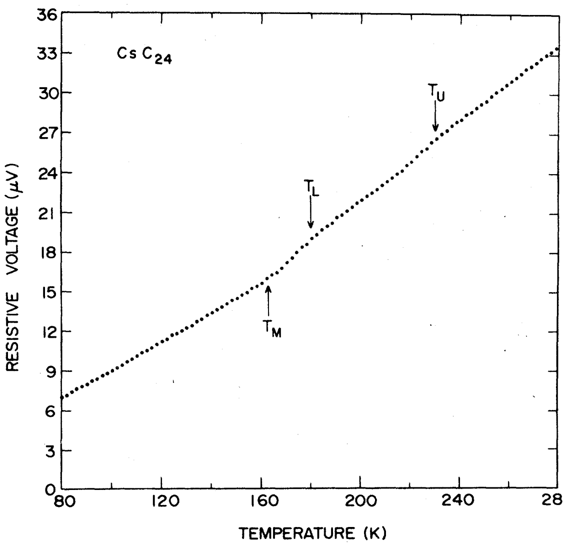

FIG. 5. Resistive voltage at constant current for CsC_{24} between 80 and 280 K. The anomalies are marked at T_U and T_L and the known order-disorder transition is at T_M.

increases to 1.8×10^{-2} $\mu\Omega\,\mathrm{cm\,K^{-1}}$. The anomalies are summarized in Table II.

(v) *Stage* 2 *rubidium graphite*: $\mathrm{RbC_{24}}$. Figure 4 shows the temperature dependence of the resistive voltage for a sample of $\mathrm{RbC_{24}}$ between 80 and 300 K. Two anomalies are apparent at 106 and 172 K having, again, the form of broadened step increases in the resistivity over regions of about 12 K. The anomalies are summarized in Table II. The temperature dependence of the resistivity is linear between T_L and T_U with a slope of 1.3×10^{-2} $\mu\Omega\,\mathrm{cm\,K^{-1}}$. Above T_U the initial slope remains the same but an added exponential contribution can be analyzed with a characteristic temperature of 750 K, corresponding to an activation energy of about 0.066 eV.

(vi) *Stage* 2 *cesium graphite*: $\mathrm{CsC_{24}}$. Figure 5 shows the temperature dependence of the resistive voltage for a sample of $\mathrm{CsC_{24}}$ between 80 and 280 K. Two anomalies are present, at 180 and 230 K, having the form of step increases in resistivity spread over about 10 to 15 K. The anomalies are summarized in Table II. The temperature dependence of the resistivity between 80 and 160 K is tending towards linear, with a slope of 1.73×10^{-2} $\mu\Omega\,\mathrm{cm\,K^{-1}}$ between 120 and 160 K. Between the anomalies the slope increases to about 2.2×10^{-2} $\mu\Omega\,\mathrm{cm\,K^{-1}}$ and has the same value, initially, just above T_U. Data did not extend to a high enough temperature to continue analysis above T_U.

B. Hall coefficient R_H and magnetoresistance coefficient M

The Hall coefficients R_H determined for *a*-axis conduction and the magnetoresistance coefficient $M(=\Delta\rho_a/\rho_{ao}H^2)$ for the samples studied are summarized in Tables III and IV for the set temperatures 4.2, 77, and 300 K, and will be discussed in detail below.

The sharpness of the resistive anomalies in $\mathrm{KC_{24}}$ led us to carry out a detailed temperature dependence study of R_H and M for this compound between 77 and 300 K. While a qualitative picture of the temperature dependence of M can be obtained by measuring resistivity versus temperature in zero field and in an applied field the effects of magnetoresistance in the thermometer prevent accurate quantitative analysis of the results. Preliminary studies of this kind were presented previously[11] and the most illus-

TABLE III. Hall coefficients R_H for *a*-axis conduction and comparison of calculated single-carrier model carrier density (n_R) with chemical composition carrier densities (N).

Material	Hall coefficient R_H at stated temperatures [$\mathrm{cm^3\,C^{-1}}$] 300 K	77 K	4.2 K	Calc carrier density $n_R(=1/R_He)$ ($\mathrm{cm^{-3}}$) 300 K	77 K	4.2 K	Chemical carrier density N ($\mathrm{cm^{-3}}$)
$\mathrm{KC_8}$	-1.45×10^{-4}	-1.1×10^{-4}	$+4.5 \times 10^{-4}$	$\sim 4 \times 10^{22}$	5.9×10^{22}	$(P)1.4 \times 10^{22}$	8.8×10^{21}
$\mathrm{KC_{24}}$	-8.8×10^{-4}	-1.23×10^{-3}	-1.6×10^{-3}	7.1×10^{21}	5.1×10^{21}	3.4×10^{21}	3.6×10^{21}
$\mathrm{KC_{36}}$	-2.5×10^{-3}	-2.3×10^{-3}	-2.1×10^{-3}	2.5×10^{21}	2.7×10^{21}	2.9×10^{21}	2.6×10^{21}
$\mathrm{KC_{48}}$	-8.0×10^{-3}	-5.9×10^{-3}	-5.7×10^{-3}	7.8×10^{20}	1.1×10^{21}	1.1×10^{21}	2.0×10^{21}
$\mathrm{RbC_8}$[a]	$\leq -6.10^{-5}$	-1.1×10^{-4}	b	$\sim 1 \times 10^{23}$	6×10^{22}	b	8.5×10^{21}
$\mathrm{RbC_{24}}$	-8×10^{-4}	-7.7×10^{-4}	b	7.8×10^{21}	8.1×10^{21}	b	3.5×10^{21}
$\mathrm{CsC_8}$[a]	$\leq -1.8 \times 10^{-4}$	-4.8×10^{-5}	b	$\sim 3.5 \times 10^{21}$	$\sim 1.3 \times 10^{23}$	b	8.0×10^{21}
$\mathrm{CsC_{24}}$	-8.4×10^{-4}	-1.9×10^{-3}	-1.9×10^{-3}	7.4×10^{21}	3.3×10^{21}	3.3×10^{21}	3.4×10^{21}
$\mathrm{CsC_{36}}$	-5.2×10^{-3}	-3.7×10^{-3}	-3.3×10^{-3}	1.2×10^{21}	1.7×10^{21}	1.8×10^{21}	2.5×10^{21}

[a] From Ref. 16.

[b] Stable value not obtained due to experimental limitations (see text).

TABLE IV. Magnetoresistance coefficients $M(=\Delta\rho/\rho_0 H^2)$ for a-axis conduction tabulated as $(M)^{1/2}$, the effective mobility, and the calculated single-carrier model carrier densities n_M.

Material	$(M)^{1/2}$ in $\mathrm{cm^2\,V^{-1}\,sec^{-1}}$ $(\equiv\bar{\mu})$			$n_M = \sigma_a / e\bar{\mu}$		
	300 K	77 K	4.2 K	300 K	77 K	4.2 K
KC_8	130	1000	1.6×10^4	6.5×10^{21}	8.4×10^{21}	1.23×10^{22}
KC_{24}	251	1800	7500	4.3×10^{21}	3.9×10^{21}	3.3×10^{21}
KC_{36}	466	2500	7600	4.5×10^{21}	6.5×10^{21}	5.5×10^{21}
KC_{48}	2300	3700	7700	6.0×10^{20}	1.5×10^{21}	2×10^{21}
RbC_8[a]	$\leq$112	1190	1×10^4	5.6×10^{21}	4.5×10^{21}	7.5×10^{21}
RbC_{24}	150	1800	b	6.3×10^{21}	2.0×10^{21}	b
CsC_8[a]	110	1070	b	5.9×10^{21}	4.6×10^{21}	b
CsC_{24}	268	1300	3770	5.1×10^{21}	4.9×10^{21}	6.2×10^{21}
CsC_{36}[a]	1380	1800	3300	5.3×10^{20}	1.6×10^{21}	1.8×10^{21}

[a] From Ref. 16.

[b] Data not available due to experimental difficulties.

trative example is reproduced in Fig. 6. From the two temperature sweeps it can be seen that the magnetoresistance is affected much more at T_L than at T_U. However, similar studies in RbC_{24} do not show such a precise differentiation between effects at T_L and T_U.[16]

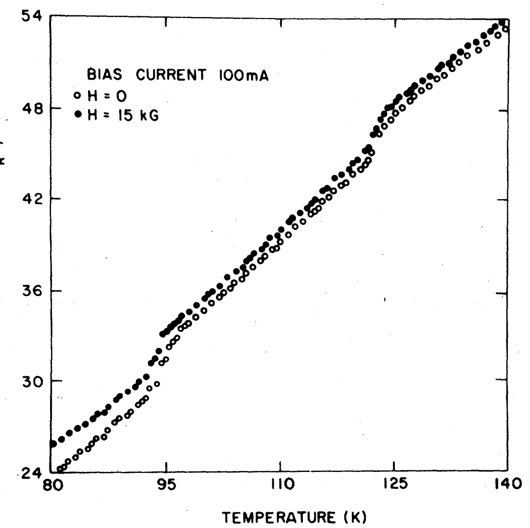

FIG. 6. Resistive voltage at constant current for KC_{24} in zero field and in a field of 15 kOe.

To obtain a clearer picture in KC_{24} we determined R_H and M very precisely from averages of eight field sweeps each using field and current reversal at a series of controlled temperatures between about 65 and 300 K. The results are shown in Figs. 7 and 8. We note that R_H is remarkably constant within experimental error (about 1.5%) from 300 down to 123 K (T_U) where it increases discontinuously by about 5%. Between T_U and T_L it remains constant at its new value. At T_L the changes are difficult to analyze since they are so abrupt, but it clear that there is a sharp change in dR_H/dT, and this may be combined with a discontinuity in R_H of between 5% and 10%. As we will discuss below, between T_L and 4.2 K R_H increases to a value that is compatible with a single-carrier electronic model for KC_{24}.

The behavior of the magnetoresistance is best illustrated by plotting $(M)^{1/2}$ (which is equivalent to an effective mobility $\bar{\mu}$) as a function of T as in Fig. 8. No discontinuity occurs in $\bar{\mu}$ at T_U or T_L but there is an increase in $d\,\bar{\mu}/dT$ on cooling through both anomaly temperatures. $d\,\bar{\mu}/dT$ is essentially constant in each of the three temperature regions.

C. Hysteresis effects and annealing

The automatic data-taking system was designed for data acquisition during warm-up only, preventing a

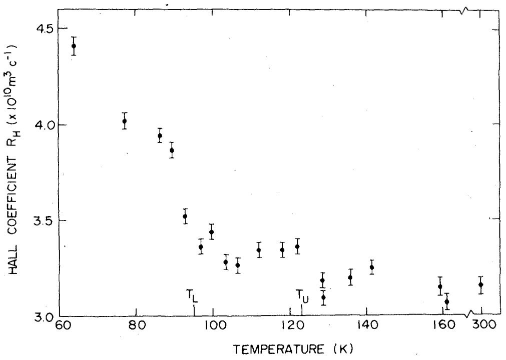

FIG. 7. Hall coefficient, R_H, as a function of temperature for KC_{24}. Note the contracted temperature scale above 160 K.

complete study of hystersis effects, but some analog data was obtained. In general the upper transition appeared to show no hysteresis effects, while the situation at the lower one was less certain and appeared to depend on the thermal history of the sample. Further careful studies are required in this area.

Generally the results obtained were consistent and repeatable many times with thermal cycling provided that temperatures did not exceed about 340 K. When a KC_{24} sample was heated above this temperature a repeat sweep to low temperatures showed that the anomaly at T_U was unaffected, while that at T_L became both much larger and much wider. Again, a careful consistent series of measurements will be required in the future, combined with parallel structural studies to examine the full effects of annealing and of the thermal history. The importance of annealing and its effects in stage 1 compounds were recently observed by neutron diffraction.[15]

IV. DISCUSSION

Preliminary measurements of σ_a, R_H, and M in selected compounds had shown that the electronic properties of stage 1 compounds at all temperatures and stage 2 compounds at 360 and 77 K cannot be described by a single-carrier model.[17] This is confirmed by the new data presented in Tables I, III, and IV. For comparative purposes we have calculated in Table III the carrier densities n_R obtained from R_H using the single-carrier model value of $1/R_He$, and compared it with the maximum carrier concentration N assuming singly ionized intercalate atoms. A similar comparison is made in Table IV using the magnetoresistance mobility $\bar{\mu}$ [$=(M)^{1/2}$] which, when combined with the conductivity, also yields an effective carrier concentration $n_M(=\sigma_a/e\,\bar{\mu})$. Disagreement between n_R and n_M suggests that the single-carrier model is inadequate, as does the condition that $n_R > N$, though the latter could occur with multiple ionization.

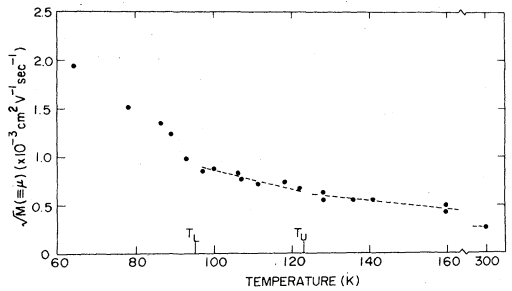

FIG. 8. $(M)^{1/2}$ $(\equiv\bar{\mu})$ as a function of temperature for KC_{24}. Note the contracted temperature scale above 160 K.

Comparison of the values of n_R, n_M, and N in Tables III and IV shows the applicability of the single-carrier model for KC_{36}, KC_{48}, and CsC_{36} at all temperatures, based on the criterion that $n_R \lesssim N$. The disagreement of n_M may arise in part from saturation effects which prevent accurate extrapolation of M to a zero-field value. KC_{24} is particularly interesting again in that a single-carrier model would be inapplicable at 77 K or above, but applicable at 4.2 K, while in CsC_{24} the single-carrier model would apply at 77 and 4.2 K but not at 300 K, again based on the $n_R \lesssim N$ criterion alone. A preliminary susceptibility study of KC_{24} however shows no strong temperature dependence and no anomalies down to 77 K which suggests that the carrier concentration in that compound is almost constant.[9]

We discuss next the relationship of the resistive anomalies to observed structural transitions before attempting to explain the temperature dependence of the electronic parameters at the anomalies.

A. Resistive anomalies and structural transitions

In Table II, and in Figs. 1, 4, and 5 we have compared our values of T_U and T_L with the temperature T_M at which various order-disorder transitions were observed in the alkali-metal layers of stage 2 compounds in the x-ray studies of Parry *et al.*[5-7] and Ellensen.[8] In each case T_M is a temperature very closely associated with T_L or T_U and in the case of the Ellensen results in KC_{24} with both T_L and T_U. In defining T_U and T_L we have used the relatively sharp upper end of the anomalies, while T_M was presumably defined by Parry as the first temperature at which disorder was apparent during warming. T_M is generally lower than T_L or T_U but, if one includes the apparent width ΔT of the resistive anomalies in the comparison, it is clear that the resistive anomalies and structural transitions are identical.

The lack of two structural transitions in the stage 2 compounds as reported originally by Parry is not an inconsistency since the early x-ray studies were not carried out extensively as a function of temperature and some order-disorder phenomena may have been overlooked.[18] The ordering observed in the metal layers in $\mathrm{RbC_{24}}$ was in fact described as incomplete, and some disorder was observed even below $T_m(\simeq T_L)$ in $\mathrm{CsC_{24}}$. New x-ray studies have already confirmed two order-disorder transitions in $\mathrm{KC_{24}}$ coincident with T_U and T_L.[8]

In an early account of part of this work[16] we considered several possible sources for the observed resistive anomalies, but now conclude that the principal source is the order-disorder transitions within the alkali-metal layers or the associated ordering between several alkali-metal layers. This conclusion is reinforced by the recent susceptibility measurement[9] which shows no anomaly larger than ±0.2% at either T_U or T_L, arguing against major Fermi-surface effects at those temperatures. The evidence from our electronic measurements, discussed in detail below, suggests that the resistivity anomalies arise from abrupt carrier mobility changes associated with the order-disorder transitions.

The source of the intralayer disorder is presumably the vacancy sites that will exist within the alkali-metal layers in the $M\mathrm{C}_{12n}(n \geqslant 2)$ compounds.[4] No such vacancies exist in the stage 1, $M\mathrm{C_8}$ compounds since the atomic packing in the metal layers is the densest possible, and indeed neither resistive anomalies nor structural reordering occurs until well above room temperature.[15] Disorder in the $M\mathrm{C_8}$ compounds can only occur by collective action of pairs of atoms, while in the more open $M\mathrm{C}_{12n}$ structure M atoms may be thermally activated to adjacent vacant sites at lower temperatures resulting in a progressively less ordered structure as the temperature increases above T_U.

B. Electronic parameters through the resistive anomalies

The temperature dependence of the electrical resistivity described in Sec. III A (Figs. 1–5) reflects the order-disorder sequence. Below T_L the resistivity behaves similarly to a crystalline metal, with a high-power dependence at the lowest temperatures, tending to a linear form by nitrogen temperature. Between the anomalies the temperature dependence remains linear, and a linear component is present for $T > T_U$. Above T_U, at least in $\mathrm{KC_{24}}$ and $\mathrm{RbC_{24}}$ for which good measurements presently exist, an exponential term seems to be added to the linear component. The exponent provides a possible measure of the activation energy associated with the proposed atomic hopping process, and is about 0.066 eV or 750 K.

Some information on the nature of the resistive anomalies themselves can be obtained from the temperature dependence of R_H and M in $\mathrm{KC_{24}}$ though conclusions may be limited to that one compound, showing, as it does, such sharp anomalies. Full quantitative interpretation is not possible because as explained above, one needs a two-carrier picture for the stage 2 materials, at least above 77 K. We cannot then obtain independent values of the two carrier mobilities (μ_e and μ_h) and two carrier densities (n_e and n_h) from the measurement of only three quantities, σ, R_H, and M. In a two-carrier model these parameters are given by

$$\sigma = 1/\rho = (n_e\mu_e + n_h\mu_h) \ , \tag{1}$$

$$R_H = \frac{1}{n_e e}\left[\frac{n_h/n_e - (\mu_e/\mu_h)^2}{(n_h/n_e + \mu_e/\mu_h)^2}\right] \ , \tag{2}$$

$$M = \frac{\Delta\rho}{\rho_0 H^2} = \frac{n_h}{n_e}\mu_e\mu_h\left[\frac{1+(\mu_e/\mu_h)}{n_h/n_e + \mu_e/\mu_h}\right]^2 \ . \tag{3}$$

In $\mathrm{KC_{24}}$ we note from Fig. 7 the constancy of R_H from 300 K down to T_U (123 K), where only a small increase occurs followed by a continued temperature-independent behavior down to 95 K. Below T_L, R_H becomes very temperature dependent until by 4.2 K the calculated carrier density would be almost consistent with a single-carrier model. The constancy of R_H over such a wide temperature range in a two-carrier system described by Eq. (2) suggests strongly that, at least down to 95 K, the carrier concentrations are constant while the temperature dependencies of μ_e and μ_h are the same. At 123 K a small change in the ratio μ_e/μ_h arising from the initiation of inplane ordering would be sufficient to explain the 5% change in R_H. Below 95 K the development of interlayer ordering, observed by Parry, would continue to affect the mobility ratio and if μ_e became much greater than μ_h the single-carrier value of R_H would obtain. The conclusions are consistent with the susceptibility results considered as a measure of the near constancy of carrier concentration.[9]

We can extend these conclusions to the temperature behavior of $(M)^{1/2}(\equiv\bar{\mu})$ for, if we assume constant carrier concentration and a near temperature independence of (μ_e/μ_h) down to T_L (except for the step at T_U) then the behavior of $(M)^{1/2}$ will be determined from Eq. (3) by the product $(\mu_e\mu_h)$. the change in $d\bar{\mu}/dT$ at 123 K (T_U) (Fig. 6) then may be attributed to a change in μ_e or μ_h alone, a conclusion consistent with that for the step in R_H at T_U. Similarly the abrupt change in $d\bar{\mu}/dT$ at T_L can be attributed to a change in both the product $(\mu_e\mu_h)$ and the ratio (μ_e/μ_h) as, for instance, μ_e becomes much greater than μ_h consistent with the explanation of the change in R_H with the development of interlayer ordering. The overall temperature dependence of the resistivity [Eq. (1)] is then attributable primarily to the temperature dependence of the carrier mobilities, and the step decreases in ρ observed at T_U and at T_L during cooling are due to mobility changes arising from the increased order of the KC_{24}.

The situation in second stage compounds other than KC_{24}, and in third and higher stages of potassium, may be more complex still since the resistive anomalies are broad rather than sharp. In addition, our qualitative scan of magnetoresistance in RbC_{24} (Ref. 16) shows that the total change in M is distributed between the anomalies at T_U and T_L. Parry and coworkers analyzed the transition they observed in RbC_{24} (for which T_m seems associated with our T_U) as due to partial inplane ordering of the alkali-metal atoms, together with some interplanar ordering. They reached similar conclusions in the case of CsC_{24} (for which T_m seems associated with our T_L), though a recent paper points out the relatively complex situation in cesium compounds arising from the fact that the ionic diameter of the cesium exceeds the available space in an interlamellar site.[19] The most complete ordering was observed in KC_{24} at 95 K where intraplanar order was complete and interplanar order extended over six metallic layers.[5–7] This variety of structural changes strongly suggests that in each compound intralayer ordering is at least initiated, but may not be completed at T_U, while interlayer ordering occurs at T_L, resulting in a different behavior of σ_a, R_H, and M for each compound.

The presence of pairs of resistive anomalies in KC_{36} and KC_{48} suggests that similar ordering sequences hold in those compounds, and one may then reasonably predict such transitions will occur in higher stages in all of the alkali-metal compounds. The variations in height, width, and overall shape of the anomalies could arise from variations in sample preparation techniques, or lack of stoichiometry though behavior has been reproducible between different samples of the same compound. The extremely narrow anomalies in KC_{24} may be the exception rather than the rule. The greater width of the resistive anomalies in all compounds except KC_{24} makes identification of changes in R_H and M very difficult to observe and analyze.

While variations of T_L and T_U between Cs, Rb, and K compounds are to be expected, it is difficult to understand the values of T_L and of T_U within the K compound sequence. One might expect that inplane ordering would occur at one temperature for all stages at T_U, while interplanar ordering might occur at varying temperatures depending on the number of graphite layers intervening between metal layers. The reverse is the case, since T_L is the same for all three K compounds studied, while T_U varies over a range of 130 K for different stages. A final conclusion will only be possible when simultaneous correlated x-ray studies and electronic studies are made on the same samples over the complete temperature range.

We note finally that, apart from their clear relevance to the understanding of the electronic properties of graphite intercalation compounds, the transitions and accompanying resistive anomalies are of interest in the general field of ordering in two-dimensional systems. Dash[20] has pointed out that in two dimensions a 2-phase coexistence region can occur for a considerable temperature range along the melting curve, and this concept was recently applied to the interpretation of the specific heat of ^4He on Grafoil.[21] The transition width that we observe at T_U and T_L (ΔT in Table II) may then be due to a gradual ordering as the two-dimensional metal layers cool along the melting curve, the latter being crossed more rapidly in KC_{24} than in the other materials studied.

V. SUMMARY

We have presented data on the overall temperature dependence of the a-axis electrical resistivity of the first stage (KC_8, RbC_8, CsC_8) and second stage (KC_{24}, RbC_{24}, CsC_{24}) graphite intercalation compounds of potassium, rubidium, and cesium, and of the third (KC_{36}) and fourth (KC_{48}) stage compounds of potassium. Hall coefficient, R_H, and magnetoresistance coefficient M, data at 4.2, 77, and 300 K were also presented for many of these compounds, and in part for CsC_{36}, together with a detailed temperature dependence for both coefficients between 65 and 300 K for the selected compound KC_{24}.

We confirm the stage 1 compounds, and the stage 2 compounds above about nitrogen temperature, require a two-carrier model to describe their electronic properties, but that for stage 2 at lower temperatures and for the higher stage compounds investigated a single-carrier model may suffice. No resistive anomalies are observed in stage 1 compounds, but in all stage 2 and higher compounds two resistive anomalies are observed at T_U and T_L. From known x-ray structure studies and recent magnetic susceptibility measurements we conclude that the anomalies are associated with intra- and interlayer ordering effects upon cooling. Such a conclusion is shown to be at least qualitatively consistent with the temperature dependence of R_H and M for KC_{24} in which compound anomalies are particularly narrow and easily studied.

The situation in the compounds other than KC_{24} is less certain, and for a complete picture to be formed it will be necessary to correlate very carefully further electronic studies and x-ray and neutron diffraction studies. The differences observed between compounds so far suggests that each may have a unique electronic description throughout the ordering process.

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