

Existence of a Magnetic Susceptibility Anomaly in the Ternary Systems $M'_{1-x}M_xC_8$

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Like the binaries, MC_8 , the ternaries $M'_{1-x}M_xC_8$ (M and $M' = K, Rb, Cs$) have a positive magnetic susceptibility which is isotropic and temperature independent. It undergoes a very drastic variation as a function of composition, for which a qualitative explanation is proposed.

I. Measurement Conditions

Potassium, rubidium, and cesium in the liquid or vapor state react with graphite to give first-stage intercalation compounds of formula MC_8 . Alloys of the heavy alkali metals under the same conditions lead to ternaries $M'_{1-x}M_xC_8$ ($0 \leq x \leq 1$).

Study of the magnetic properties of such compounds possessing quasi-free electrons is an investigation necessarily preceding more elaborate experiments concerning cyclotron resonance and the de Haas-Van Alphen effect. The values of magnetic susceptibility given in the literature concerning the binaries KC_8 and RbC_8 (1, 2) are quite dispersed. It seems that the method of preparation is the essential cause of these differences. No measurement had yet been undertaken on the ternaries $M'_{1-x}M_xC_8$.

The samples were prepared using natural graphite from Ceylon from which all ferromagnetic impurities were removed (grain

size comprised between 200 and 300 μ). The formulas of the compounds were determined by weighing the starting graphite (about 100 mg) and the intercalated metal. The error in x is of the order of a few one hundredths.

The magnetic susceptibility of the compounds, kept in sealed tubes, was measured using the Faraday method (3). The sensitivity of the apparatus utilized allows knowing the susceptibility to a high degree of precision ($\Delta\chi = \pm 5 \cdot 10^{-8}$ emu cgs g^{-1}). The thermal variation of the susceptibility was studied for several compounds between 77 and 300 K.

Whether or not the graphite was diluted in alumina, the results obtained on several compounds were identical within experimental error. It thus seems that the magnetic anisotropy, notable in the case of the starting graphite, is sufficiently low after intercalation, so that the measurements are significant.

II. Results

(a) The Binaries MC_8

These compounds are slightly paramagnetic. Figure 1 shows that the susceptibility of KC_8 , RbC_8 , and CsC_8 does not vary down to the temperature of liquid nitrogen.

Table I shows the results of our measurements and allows us to compare our values and those calculated starting with the measurements of Fishers *et al.* In spite of the drastic anisotropy indicated by the latter authors, the values of the average susceptibility are in good agreement for the three binaries. However, the discrepancies observed may be attributed to the important relative error (about 50%) measured by these authors on the χ_{\perp} values.

The passing from an initial diamagnetic susceptibility to Pauli paramagnetism after intercalation of a heavy alkali metal is interpreted in Section III.

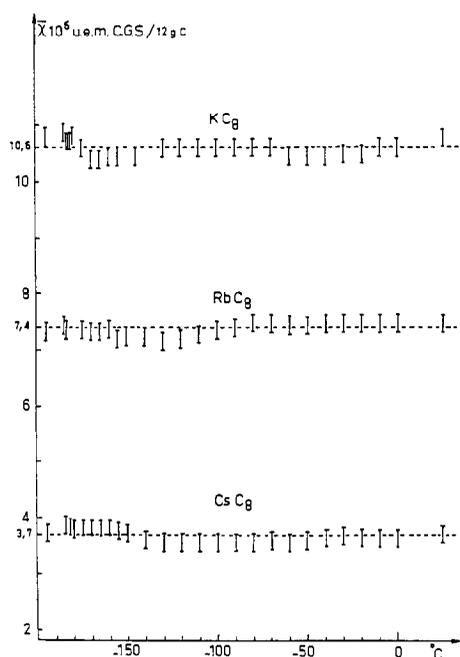


FIG. 1. Magnetic susceptibility of MC_8 compounds as a function of temperature.

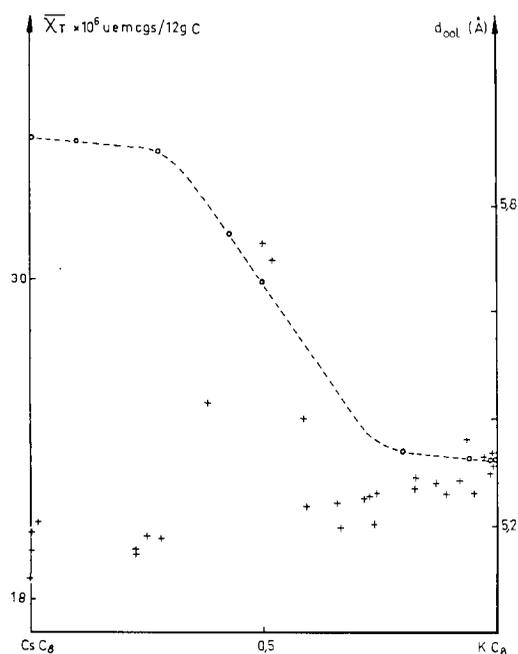


FIG. 2. Variation of $\bar{\chi}_T$ and d_{\perp} as a function of x in the system $Cs_{1-x}K_xC_8$.

(b) The Ternaries $M'_{1-x}M_xC_8$

Variation of the susceptibility with the composition has been studied for three ternary systems:

graphite-potassium-cesium
graphite-potassium-rubidium
graphite-rubidium-cesium

Let us define χ_T as being the magnetic contribution of the s electrons of the intercalated metallic layer. We will insist upon this definition in the following paragraphs. Figure 2 shows the evolution of $\bar{\chi}_T$ as a function of the proportion of potassium in a

TABLE I

Formula	$\bar{\chi}_{\text{meas.}} \times 10^6$ 1 mu cgs/12 g of carbon	$\bar{\chi}_{\text{cal.}} \times 10^6$ 1 mu cgs/12 g of carbon
KC_8	10, 6	8, 9
RbC_8	7, 4	5, 7
CsC_8	3, 7	4, 5

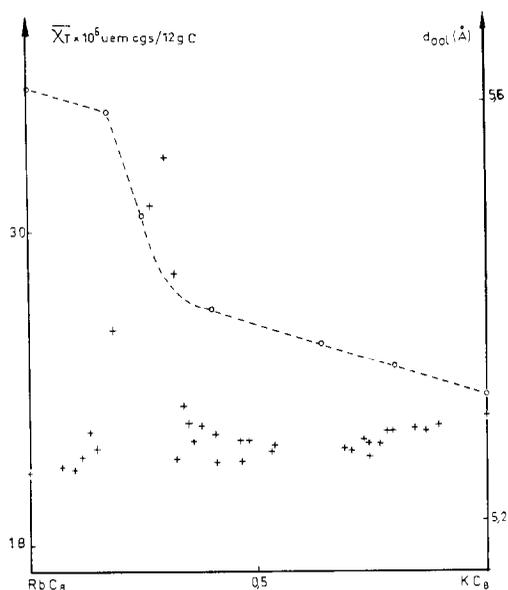


FIG. 3. Variation of $\bar{\chi}_T$ and d_i as a function of x in the system $Rb_{1-x}K_xC_8$.

potassium-cesium alloy. The dispersion of the points on the side of alloys rich in cesium is undoubtedly explained by the miscibility of the cesium suboxides in the metal. On the side of the potassium-rich alloys, the variation of $\bar{\chi}_T$ with x is linear. Around $x = \frac{1}{2}$ there appears a large variation of the susceptibility followed by a leveling off toward CsC_8 .

Figure 3 shows the evolution of $\bar{\chi}_T$ as a function of the proportion of potassium in a potassium-rubidium alloy. The general shape of the curve is the same as the preceding one. The position of the anomaly is displaced towards the rubidium. The sudden variation in $\bar{\chi}_T$ appears towards $x = 0.4$.

Figure 4 shows the variation of $\bar{\chi}_T$ with x for the ternaries $Cs_{1-x}Rb_xC_8$. There is no disruptive change of $\bar{\chi}_T$ in the system. Nevertheless, for x comprised between 0.7 and 0.9, the curve presents a protuberance.

Note that in the three systems, the susceptibility peak appears in the zone where the curve of the variation of interplanar

TABLE II

Formula	$\bar{\chi}$ 300 K	$\bar{\chi}$ 77 K
$K_{0.66}Cs_{0.34}C_8$	7, 39	7, 37
$K_{0.38}Cs_{0.62}C_8$	11, 48	11, 48
$K_{0.5}Cs_{0.5}C_8$	17, 76	17, 75
$K_{0.3}Rb_{0.7}C_8$	19, 74	19, 74

distance with x possesses an inflection point (4). This is discussed in Section IIIb.

Table II shows that the susceptibility of several ternaries does not vary between 77 and 300 K. This study was in particular done for compounds found in the zone of the anomaly.

III. Interpretation of the Results

(a) Calculation of Magnetic Susceptibility for the Ternaries

The magnetic susceptibility of the compounds studied is the sum of four terms:

—The orbital diamagnetism of the electrons bound to the atoms or *the Langevin*

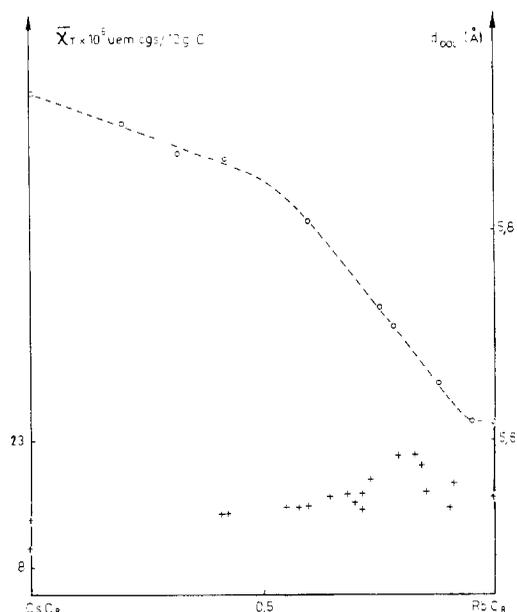


FIG. 4. Variation of $\bar{\chi}_T$ and d_i as a function of x in the system $Cs_{1-x}Rb_xC_8$.

diamagnetism. This diamagnetism is roughly isotropic and does not depend on the temperature. It is of the order of magnitude of the susceptibility parallel to the graphite planes increased by the diamagnetic contribution of the "alkali ions." This is so if the ionization of the alkalis is complete; the electrons of the ion are all paired, the electron freed by ionization finding itself a quasi-free conduction electron. If the ionization were not complete, a certain number of the electrons would not be paired and in the absence of any alkali-alkali or alkali-graphite bond, would introduce a Curie paramagnetic susceptibility, variable with the temperature. The results given above, however, show that this contribution exists neither in the binaries nor in the ternaries within the limits of experimental error (the measurements are to within 1%).

—The anisotropic *London susceptibility* due to the π electrons ($\Delta\chi_\pi$).

— χ_p , the isotropic susceptibility of the free electrons or the *Pauli paramagnetism*. This term shows the proportion of electrons parallel and antiparallel to the magnetic field.

— χ_a , the anisotropic diamagnetic susceptibility of the free electrons, or Landau diamagnetism (5, 6). This term arises from the modification of the electronic orbital motion energy in the presence of a magnetic field: for a free electron gas $\chi_a = -\chi_p/3$.

The effect of the lattice field can be included through an "effective electronic mass" $m^* = m/\alpha$: then, for quasi-free electrons

$$\chi_p \text{ is proportional to } 1/\alpha,$$

$$\chi_a \text{ is proportional to } \alpha,$$

$$\chi_a = -\alpha^2\chi_p/3.$$

If α is large, χ_p can be neglected in comparison with χ_a .

If α is small, χ_a can be neglected in comparison with χ_p .

It will be seen that the experimental values of $\bar{\chi}$ imply quite small values of α . Then the Landau diamagnetism is practically quite negligible and the total free electron susceptibility χ_T is paramagnetic.

Moreover there is some doubt about the necessity of including both the London susceptibility and the free electron term in the total value of $\bar{\chi}$, since the Landau diamagnetism in graphite clearly arises from the same origin as the London anisotropy in aromatic compounds, when the π electrons move more and more freely along the aromatic network.

Then the free electron susceptibility $\bar{\chi}_T$ may be used as representing the total π electron contribution to the average susceptibility of a compound $M'_{1-x}M_xC_8$:

$\bar{\chi}$ measured

$$= -(8\chi_C + x\chi_M + (1-x)\chi_{M'}) + \bar{\chi}_T$$

In the discussion which follows the experimental results $\bar{\chi}$ are corrected for the atomic and ionic diamagnetic contributions:

$$\chi_C = -0,35 \times 10^{-6} \text{ em cgs g}^{-1}$$

$$\chi_{K^+} = -0,33 \times 10^{-6} \text{ em cgs g}^{-1}$$

$$\chi_{Rb^+} = -0,23 \times 10^{-6} \text{ em cgs g}^{-1}$$

$$\chi_{Cs^+} = -0,23 \times 10^{-6} \text{ em cgs g}^{-1}$$

in order to determine the value of $\bar{\chi}_T$.

(b) Discussion and Proposition of an Electronic Model

The binaries. Starting from the measurements of susceptibility corrected for the diamagnetic effect of the bound electrons, we have calculated the term $\alpha = m/m^*$ taking into account the properties of the quasi-free electrons. The calculations have been carried out for the free metal and the intercalated metal respectively based on

TABLE III

α	K	Rb	Cs
Free metal	0.582	0.569	0.451
Intercalated metal	0.208	0.232	0.258

the measurements of Klemm (7) and Furdin (8). Table III shows the results.

The apparent mass for the free metals is approximately twice of the electron mass. For the intercalated metals, the apparent mass is systematically higher and decreases from potassium to cesium.

It is tempting to relate the variation in α to the number of the electron shell and the reactivity of the alkali metal with respect to graphite; this latter parameter increases in going from potassium to cesium.

We have intentionally not wanted to go further in the interpretation of the apparent electron mass. While it is theoretically possible to describe this through perturbation theory, various correlation and exchange phenomena are liable to modify the real density of states on the Fermi surface and thus the determination of α . Valuable experiments using quantum oscillation effects should allow taking into account these factors and going further in the exploitation of the experimental results.

The ternaries. Let us note that the powder X-ray diffractograms of these ternaries evolve regularly as a function of the composition; the interplanar distances and the intensities of the reflections vary but not their number.

The atoms M and M' have different volumes: their simultaneous intercalation into graphite does not modify the nature of the lattice but changes the parameter corresponding to the distance between the graphite planes. Figures 2-4 also show the variation in interplanar distance with composition in the compounds $K_xCs_{1-x}C_8$, $K_xRb_{1-x}C_8$. Vegard's law is not respected

and it is necessary to attain a certain value of substitution before the interplanar distance starts to vary rapidly with the composition. The alkali metals intercalated between the graphite layers can therefore become deformed; if not, the interplanar distance of a ternary would be equal to that of the compound containing the larger atom. Thus it would seem that the ternaries $M'_{1-x}M_xC_8$ are disordered solid solutions of the binaries MC_8 and $M'C_8$ (4, 9).

Thermodynamic studies confirm this conclusion showing that the difference from the ideal situation is almost nonexistent in the ternaries $Rb_{1-x}K_xC_8$ and $Cs_{1-x}Rb_xC_8$ and low for $Cs_{1-x}K_xC_8$ (10).

In the first stage compounds KC_8 and RbC_8 , the metallic atoms successively occupy the four sites which are available to them. Lagrange and co-workers have shown the presence of three different orthorhombic cells, belonging to the space group $Fddd$, shifted with respect to each other by an angle of 120° (11, 12). On the other hand, in CsC_8 , the cesium atoms occupy only three of the four possible sites. The compound therefore comprises six hexagonal cells shifted from each other by an angle of 60° and broken into two groups of enantiomers, respectively, belonging to space groups $P6_222$ and $P6_422$ (13).

Therefore, the small differences between the structures common to KC_8 and RbC_8 on one hand, and to CsC_8 on the other, do not allow explaining the magnetic anomaly since it also appears in the system KC_8 - RbC_8 .

The existence of a superstructure would furnish a better explanation, but without being totally excluded, it cannot for the moment be retained, due to lack of experimental proof.

The temperature-independent paramagnetism of the binaries and ternaries can only be explained by a delocalization of the s electrons of the intercalated alkali atoms. This delocalization can be effected either at

the interior of the intercalated metallic layer or, on the contrary, by a transfer to the adjacent carbon layers, or by both. In the first case, the intercalated layers are of the metallic type; in the second case, they are of the ionic type. The two possibilities have been envisaged and have led to two different interpretations.

The metallic model based on the study of a single band is particularly simple and has allowed a qualitative approach to the phenomena (8). The magnetic anomaly encountered in the three ternary systems would arise from a sudden variation in the density of occupied states in the conduction band of the intercalated alkali metal. Each intercalated metal layer can be considered as constituting a bidimensional conductor and the formulas for the magnetism of a bidimensional electron gas can be applied. If it is admitted that the transfer of electrons from the alkalis to the carbon is only partial and leads, on one hand, to the disappearance of the diamagnetism of the graphite and, on the other hand, to the existence of Pauli paramagnetism in the metallic bidimensional layers, it can be shown that a small decrease in thickness of the metallic layers can lead to a drastic increase in the density of occupied levels, and thus to the magnetic anomaly. This decrease is precisely that which is observed in the zone of concentrations where the ternary does not obey Vegard's law.

In this article, we present different hypotheses leading to an "ionic model," explaining the magnetic anomaly by the transition of the smaller metallic atoms from the ionic to the metallic state.

A ternary compound $M_{1-x}M'_x C_8$ (M being the smaller and M' the larger alkali atom) may be obtained by the progressive substitution of M in the binary $M'C_8$. At the beginning of the process, the M' atoms in $M'C_8$ are assumed to be completely ionized, and all their s -band free electrons are transferred into the π conduction band of

graphite, where they have a high density of states (or effective mass) at the Fermi level. Thus all the observed paramagnetism arises from these π electrons, and also possibly from covalent bonds between the carbon and metal atoms.

When M atoms are substituted, the crystallographic sites which are offered them are too large, both along the layer planes (for K atoms) and perpendicular to the planes (for K as well as Rb). Because of their smaller size they create lower levels in the s conduction band: this goes on as long as the distance between the carbon layers does not decrease significantly. So that the bottom of the s band gets lower and lower as more and more M atoms are introduced. For a critical value of x , the bottom of the s band falls below the Fermi level and the band starts filling up. From this point on the alkali atoms ionization is no longer complete. The Fermi level is lying both in the π band of graphite and in the s band of the metal atoms. An additional contribution to the paramagnetism arises from the s band. It gets larger as the electron effective mass (or density of states) increases at the Fermi level, because of the progressive "sinking" of the s band.

But this process is reversed when more and more M' atoms are replaced by smaller M atoms and the distance between carbon layers starts decreasing rapidly: the M' atoms are "squeezed" and the M atoms have less "extra space." This results eventually in a rising of the s band as the potential wells of the alkali atoms become shallower. The paramagnetic contribution of the s band reaches a maximum and then decreases. It vanishes when the Fermi level falls below the bottom of the s band. The ionization of the alkali atoms is once more complete and will remain so as the last M' atoms are replaced and the ternary compound changes into the binary MC_8 . Thus the maximum of the magnetic anomaly coincides with the fastest decrease of the

interplanar distance, as shown by Figs. 2–4.

The metallic rubidium lattice adapts itself quite well to that of graphite. The disposition of the Rb^+ ions in an intercalated layer of RbC_8 is practically the same as that of the ions or atoms in a (101) plane of the metal. On the other hand, the Cesium lattice is retracted and that of Potassium is dilated when these metals are intercalated. Then the s electrons of intercalated Cs and K must have effective masses, respectively, inferior and superior to that of Rb: Table III shows that it is indeed so.

This model also allows a prediction of the relative shifts of the anomaly. Starting from CsC_8 , the fastest decrease of the interlayer distance is reached at a smaller x value for K and a larger value for Rb substitution since K is smaller than Rb: then the anomaly maximum for K is at $x = 0.5$ which is smaller than the Rb value ($x = 0.8$). Conversely, starting from KC_8 , the fastest increase of the interlayer distance corresponds to a larger concentration of substituted Rb and a smaller concentration of Cs: then the maximum of the anomaly for Rb is at $1 - x = 0.65$ which is larger than the Cs value ($1 - x = 0.5$).

It is also quite understandable that the size of the anomaly is much smaller in the Cs–Rb compound since the Rb atoms fit very well in the intercalated layer plane: their potential wells are not so deep as those of K atoms which are too small for the space offered them in the metallic two-dimensional lattice, either in the Cs–K or the Rb–K compounds. Then the overflow of the Fermi level in the s band is certainly much more important in the latter compounds than in $Cs_{1-x}Rb_xC_8$ and the corresponding paramagnetic contribution is larger.

IV. Conclusion

Study of the ternaries $M'_{1-x}M_xC_8$ has

shown a sudden variation in the paramagnetism due to the free electrons as a function of the composition. This type of anomaly does not seem to have been previously observed. The qualitative explanation which is proposed requires being tested by the experimental study of other electronic properties and confronted with works concerning band structures when they are sufficiently well determined. Without rejecting the metallic model which led us to relatively simple mathematical developments, the ionic model appears to us to be more satisfactory. New experiments will allow determining with greater precision the nature of the bonds in these compounds and will permit choosing one or the other of these models.

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