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Dimensionality of Superconductivity in Graphite Lamellar Compounds*

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The occurrence of superconductivity in some of the alkali-metal–graphite lamellar compounds, and its absence in others, has been used as evidence against the existence of two-dimensional superconductivity. In this paper we explain the different superconducting transitions of these compounds in terms of the different carrier populations in the planes and show that no conclusion can be reached about two-dimensional superconductivity.

SUPERCONDUCTIVITY in the alkali-metal–graphite compounds[1–4] has been reported by Hannay *et al.*, hereafter referred to as HGMASM.[5] In this paper we are concerned with one particular aspect of this work, namely, the question of the possibility of two-dimensional superconductivity. The question of the possible existence of two-dimensional superconductivity was first raised by Ginzburg and Kirzhnits.[6] In a paper concerned mainly with superconductivity of electrons in the surface of a metal or a dielectric, they discussed the possibility of two-dimensional superconductivity and indicated that in a two-dimensional system a resultant attraction between particles should lead to a gap in the one-particle excitation spectrum. However, recently, Rice[7] has indicated that Yang's[8] criterion for long-range order is not satisfied in one and two dimensions. Hence, the question of whether alkali-metal–graphite compounds constitute a two-dimensional system is an important one. In a series of important experiments, HGMASM found that the yellowish compounds having the general formula C_8M (M represents K, Rb, or Cs) are superconducting, whereas the blue compounds, identified by them as $C_{16}M$, are not superconducting down to 0.011°K. In the compounds C_8M, the alkali metal is interleaved between every pair of adjacent graphitic layers. These metal atoms form a triangular network in each layer in which the centers of alternate carbon hexagons contain alkali-metal atoms [see Fig. 1(a)]. HGMASM indicate that in the compounds $C_{16}M$ the alkali-metal atoms are located in the alternate spaces between the graphitic-layer planes, and not all adjacent pairs of graphitic layers are connected by alkali-metal atoms. Also, this assumes that the density of metal atoms in the layers of $C_{16}M$ is the same as in C_8M. It is suggested by HGMASM[5] that if two-dimensional superconductivity occurred in the hexagonal planes perpendicular to the c axis, one would expect that interconnections along the c axis would not be crucial. They indicate that, for this case, T_c for the compounds $C_{16}M$ should not be greatly different from the values for C_8M. However, the preliminary results quoted in their paper showed more than an order-of-magnitude difference between the respective transitions, and that the transitions of the blue compounds, identified by them as $C_{16}M$, lie below 0.011°K. Because the c-axis connections did appear to have a crucial effect on their results, the argument of HGMASM implies that these data are evidence against the existence of two-dimensional superconductivity.

In this paper reasons are given why the superconductivity data for these graphite lamellar compounds cannot be used as an argument against or in favor of

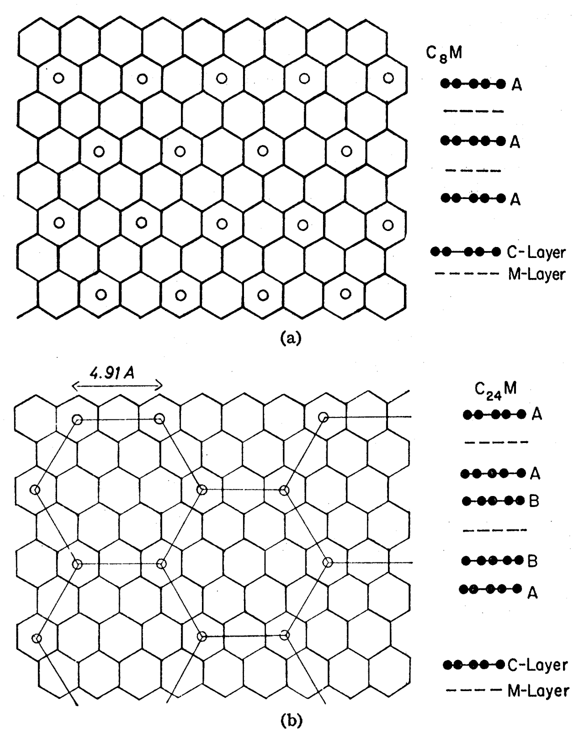

FIG. 1. Structure of the alkali-metal–graphite compounds: (a) C_8M, (b) $C_{24}M$.

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[2] W. Rudorff, Advan. Inorg. Chem. Radiochem. **1**, 223 (1959) (see especially p. 236).
[3] A. R. Ubbelohde and F. A. Lewis, *Graphite and Its Crystal Compounds* (Clarendon Press, Oxford, England, 1960).
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[8] C. N. Yang, Rev. Mod. Phys. **34**, 694 (1962).

the existence of two-dimensional superconductivity. Our argument rests on the evidence that the formation of these lamellar compounds involves charge transfer from the alkali metal to the graphitic layers[9] and that conduction occurs, as suggested by HGMASM, in the hexagonal planes perpendicular to the c axis. With these assumptions it can be argued that the differences in superconducting properties of the yellow and blue compounds can be explained by the differences in the number of conduction electrons in the conducting planes.

If the density of alkali metal in the filled layers is essentially the same in the blue and yellow compounds,[10] then there may be twice as many electrons donated to each graphitic layer in C_8M compared with the blue compounds. This is likely because each graphitic layer in C_8M has alkali-metal atoms on both sides, whereas the graphitic layers in the blue compounds have alkali-metal atoms on only one side. This is then sufficient to explain the larger T_c in C_8M because of the larger number of carriers which may be introduced by charge transfer from the two adjacent alkali-metal layers. Hence, to summarize, if charge transfer takes place, the difference in T_c between the blue and yellow compounds can easily be explained through the usual BCS formula[11] $kT_c \sim 1.14\langle\hbar\omega\rangle \exp\{-1/NV\}$ by considering the effect of a factor of 2 difference in the carrier population on NV in the superconducting regions of the two compounds. In view of this simple possibility of a large difference in the number of carriers in the hexagonal planes of the blue and yellow compounds and a corresponding change in the transition temperatures, one cannot argue that the absence of superconductivity in the blue compounds is due to the lower number of alkali-metal layers in the c-axis direction which gives these compounds a more two-dimensional nature than the yellow compounds.

Lastly, we would like to point out that the blue compounds identified by HGMASM as $C_{16}M$ are actually $C_{24}M$. It has been established that $C_{16}M$ does not exist in the cesium- or rubidium-graphite systems.[1,2,12] Rudorff[2] and Hennig[1] also indicate that $C_{16}M$ has not been found in the potassium-graphite system. The blue compounds which were thought to be $C_{16}M$ were most likely $C_{24}M$. The structure of $C_{24}M$ is shown in Fig. 1(b) where it is seen that the density of the alkali-metal atoms in the filled layers is $\frac{2}{3}$ the value of the C_8M structure. The alternating sequence of filled and empty layers in $C_{24}M$ is the same as in the assumed $C_{16}M$ structure. Hence, even in the improbable case of superconductivity in isolated alkali-metal atom planes, one can offer an explanation for the difference in T_c between the blue and yellow compounds which involves the different density of alkali-metal atoms in the planes. Again, because of this simple alternative possibility to explain the different T_c's of these compounds, the present data cannot be used to determine whether the absence of superconductivity in the blue compounds is due to their more two-dimensional character compared to the yellow compounds.

In summary, superconductivity has been observed in these highly two-dimensional systems. This is evidenced by the anisotropy of the electrical resistance in the normal state,[13] the angular dependence of the critical field,[5] and, of course, the structure.[2] Because the bonding in these compounds probably involves charge transfer between alkali-metal atoms and graphite layers, and also weak interactions between alkali-metal–filled layers,[14] these systems are probably not strictly two dimensional. However, they are probably the most two-dimensional structures in which superconductivity has been observed, and the properties of these systems therefore deserve further study. Even more interesting from the point of view of two-dimensional superconductivity are the suggestions of HGMASM that superconductivity might occur in planes perpendicular to the c axis and that these compounds open the way to further studies bearing on the possible existence of two-dimensional superconductivity. In this regard, it is of special interest to determine whether two-dimensional systems achievable in the "real" physical world can be superconducting, in contrast to the theoretical predictions of the nonexistence of superconductivity in a mathematical plane.

ACKNOWLEDGMENTS

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[9] The mechanism of bonding in these compounds involves an electron-transfer mechanism and the electrons donated to the graphitic layers have a significant effect on normal conduction in these layers (Ref. 1).

[10] In the discussion to follow it is indicated that the blue compounds have 33% fewer atoms in the metallic planes.

[11] V. L. Ginzburg [Phys. Letters **13**, 102 (1964)] indicates that the BCS result, that $kT_c \sim 1.14\langle\hbar\omega\rangle \exp\{-1/NV\}$, can be used in the two-dimensional case. This is implicit in the discussion.

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[13] L. C. F. Blackman, J. F. Mathews, and A. R. Ubbelohde, Proc. Royal Soc. (London) **A258**, 339 (1960).

[14] The heats of formation of the last four stages in the cesium- and rubidium-graphite systems become less negative as the distance between adjacent alkali-metal layers decreases. This is probably a result of an increasing interaction between the filled layers.