Mechanism of Superconductivity in Graphite Intercalation Compounds (GICs)

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In the study of the superconducting transition temperature T_c by *ab initio* calculations, the ultimate goal is to predict T_c by using only the information on elements composing superconductors. A less ambitious and yet very important goal is to make an accurate estimation of T_c directly from a microscopic Hamiltonian (in particular, without resort to the concept of the Coulomb pseudopotential μ^*), which helps us not only better understand the mechanism of superconductivity but also obtain valuable hints to synthesize a room-temperature superconductor.

In pursuit of the latter goal, a proposal was made in 1978 for a scheme of calculating T_c directly from the dynamic electron-electron effective interaction $V(\boldsymbol{q},\omega)$, including both the phonon-mediated attraction and the Coulomb repulsion on the same footing [1]. The scheme was successfully applied to the *n*-type semiconducting $SrTiO_3$ in which polar-coupled phonons leading to the stress-induced ferroelectrics were clarified to play a crucial role [2]. This success has assured us of both usefulness of this scheme and adequacy to employ the random-phase approximation in determining $V(\boldsymbol{q},\omega)$ in the polar-phonon mechanism. In 1982 this scheme was also successfully applied to the alkali-doped GICs such as KC_8 and RbC_8 with T_c in the range 0.01-0.1K by adopting such a model for the GICs as schematically shown in Fig. 1 [3].

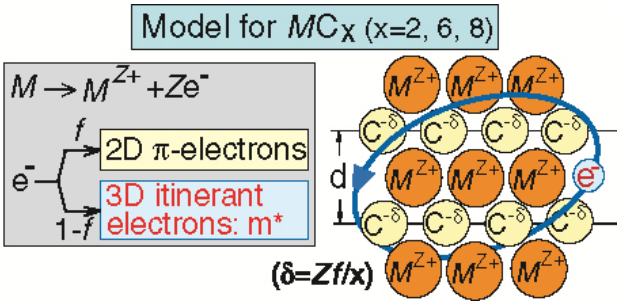

Fig. 1. In the GICs denoted by MC_x, the metal element M is ionized into M^{Z+} with Z the valence. The valence electrons released from M go into either the two-dimensional (2D) π-bands on the graphite layers or the three-dimensional (3D) interlayer band with the branching ratio of f : (1 - f). The 3D electrons with the effective mass m^* superconduct with the formation of the Cooper pairs mediated by the polarization waves of ions.

In 2005, a breakthrough occurred in the field of the GIC superconductors. By changing alkali dopants into alkaline-earth ones in synthesizing the GICs, T_c was found to be very much enhanced. In CaC_6, for example, T_c=11.5K, which was increased further to 15.1K under pressures, and in YbC_6, T_c=6.5K. Note that T_c in CaC_6 is about a hundred times higher than that in KC_8, though the ion masses are about the same.

In order to check whether the same model in Fig. 1 applies to the newly-synthesized alkaline-earth-doped GIC superconductors or not, we have recently calculated T_c based on exactly the same scheme [4]. The parameters in the model have been changed appropriately for the new superconductors; for example, we have used Z=2 instead of Z=1, m^*~3m_e (due to the mixing of d electrons with the interlayer band) instead of $m^*=m_e$ (m_e: the mass of a free electron) and f = 0.16 (reflecting the stronger attractive potential of M^{2+} for the interlayer band) instead of f = 0.6. As shown in Fig. 2, we find that our calculations reproduce all the experimental results quite well, implying that our model must be a standard one representing all GIC superconductors with T_c ranging more than three orders of magnitude. Our calculations also reveal that the key parameters to control T_c are Z and m^*; the difference in T_c by two orders between KC_8 and CaC_6 can be accounted for by (1) doubling Z, which enhances T_c by one order, and (2) tripling m^*, which also enhances T_c by one order.

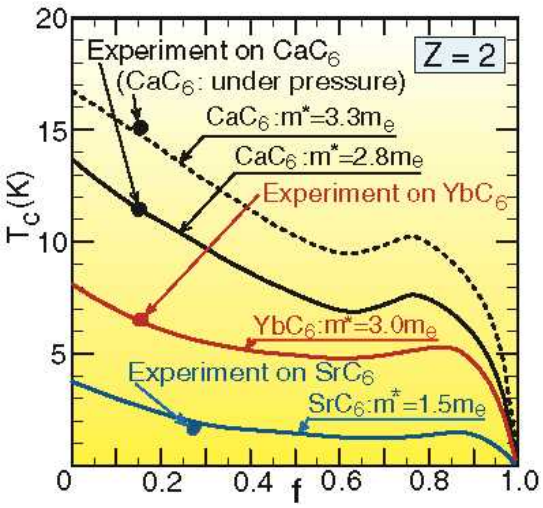

Fig. 2. Calculated T_c as a function of the branching ratio f. The calculation is done from first principles based on the model in Fig. 1 with using the band mass of the 3D electrons for m^*. The experimental result of T_c for each GIC is plotted at the value of f determined by the band-structure calculation.

Encouraged by this success and with confidence in the predictive power of our standard model, we have estimated the optimum T_c in the GIC superconductors to find that T_c may become much higher than 10K, if M is chosen as Ti or V. A further enhancement of T_c, which might enter the range 50-100K, can be expected, if two or more kinds of Ms are suitably intercalated, so that both m^* and Z are made large enough and the polar-phonon energy is made as large as possible.

References

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