

## Thermodynamics of the $d$ -wave pairing in organic superconductors

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Organic superconductors with  $\kappa$ -type structure are most frequently identified as nodal gap superconductors from the experimental observation of a power-law behavior in the low-temperature thermodynamic properties such as specific heat capacity. We perform series of theoretical calculations of specific heat capacity of three typical organic complexes with different transition temperatures by using Bogolyubov–de Gennes equations. The good agreement between the experimental data and the calculations demonstrates that the  $d$ -wave pairing is certainly realized in these superconductors.

*Keywords:* Organic superconductors; thermodynamics; specific heat;  $d$ -wave pairing.

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### 1. Introduction

The physics in organic charge transfer complexes are attracting growing interests, since they give a variety of electronic phenomena and phase transitions in low energy region in relatively clean lattices. In these complexes, the organic  $\pi$ -electrons generally have narrow band structures with low-dimensional character

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which sometimes compete with other factors such as electron correlations and electron–phonon interactions. Therefore, the superconductivity in organics is very interesting in terms of their pairing mechanism and novel possibility to produce exotic features peculiar for molecular materials. Thermodynamic measurements of organic superconductors can give information on the phase transitions and quasi-particle excitations from the pairing ground state.<sup>1</sup> A number of experiments suggest the occurrence of the unconventional superconducting state in them. The unconventional feature of the superconductivity is characterized by a structure of the superconducting gap with nodes along certain direction of the Fermi surface. The organic molecular compounds namely  $\kappa$ -(ET)<sub>2</sub>X are known as very anisotropic quasi-two-dimensional superconductors of which transition temperatures are close to 12 K known as the maximum temperature of organic superconductors. It was pointed out earlier that many anomalous normal state properties of layered organics strongly suggest the important role of electronic correlations as well as electron–phonon interactions and that some of these anomalous are in striking similarity to cuprate superconductors.<sup>2–4</sup>

The purpose of this paper is to show the measurements and calculation of the thermodynamic properties of the three typical organic superconductors with  $\kappa$ -type structures. The low-temperature thermodynamics of superconductors is determined by excitation of two quasiparticles. In the traditional superconductors with pairing of BCS-type, the energy gap is isotropic, and the temperature dependence of the specific heat capacity has an exponential form. In the superconductors with anisotropic pairing, the temperature dependence of the specific heat capacity has a power character  $T^n$ . The appearance of such temperature dependence is related to the fact that the superconductivity gap has zeros on the Fermi surface.<sup>5</sup> It was shown in Refs. 6–9 that the thermodynamics of cuprate superconductors can be successfully described by the  $d$ -pairing so that the power rule holds. We will calculate the specific heat capacities for the three compounds of organic superconductors with the  $k$ -type structure, by using the Bogolyubov–de Gennes method.

## 2. Model

We use Bogolyubov–de Gennes equations:

$$\begin{cases} \left( -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) - \mu \right) u(\mathbf{r}) + \Delta(\mathbf{r})v(\mathbf{r}) = Eu(\mathbf{r}), \\ \Delta^*(\mathbf{r})u(\mathbf{r}) - \left( -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) - \mu \right) v(\mathbf{r}) = Ev(\mathbf{r}), \end{cases} \quad (1)$$

where  $\Delta$  is the superconducting gap ( $\Delta = \Delta(T, \varphi)$ ), and  $\mu$  is the chemical potential.

Equation (1) can be interpreted as a wave equation for the two-component wave function  $\hat{\Psi}(\mathbf{r}) = \begin{bmatrix} u(\mathbf{r}) \\ v(\mathbf{r}) \end{bmatrix}$  of a quasiparticle with energy  $E$ . The superconductivity gap will be set “by hand” in the form of the pure  $d$ -wave pairing, which will allow us to solve the problem sufficiently exactly.

We will study the Bogolyubov–de Gennes equations by using a numerical method. The calculation algorithm is realized with the use of the most powerful FORTRAN language specially developed for mathematical calculations.

### 2.1. *d*-wave pairing

We have used the model proposed in Ref. 8 for the extended *d*-wave pairing of cuprate superconductors, by adapting parameters for organic superconductors.<sup>1</sup>

The extended *d*-wave gap can be written as

$$\begin{aligned} \Delta(T, \varphi) &= \Delta(T)g(\varphi), \\ g(\varphi) &= B \cos(2\varphi) + (1 - B) \cos(6\varphi), \\ \Delta(T) &= \delta \tanh \left( \frac{\pi}{\delta} \sqrt{c \left( \frac{T_c}{T} - 1 \right)} \right). \end{aligned} \tag{2}$$

For a pure *s*-wave, we have  $g(\varphi) = 1$ .

For a pure *d*-wave, we take  $B = 1$  (Fig. 1) and hence

$$g(\varphi) = \cos(2\varphi). \tag{3}$$

We will use this formula for pure *d*-wave pairing in our calculations.

The specific heat capacity in the superconducting state is given by the formula

$$C_v \equiv T \left( \frac{dS}{dT} \right) = \sum_k \frac{1}{2} k_B \beta^2 \left[ E_k + \beta \left( \frac{dE_k}{d\beta} \right) \right] E_k \operatorname{sech}^2 \left( \frac{\beta E_k}{2} \right). \tag{4}$$

where  $\beta = 1/k_B T$  and  $E_k$  is the energy spectrum.

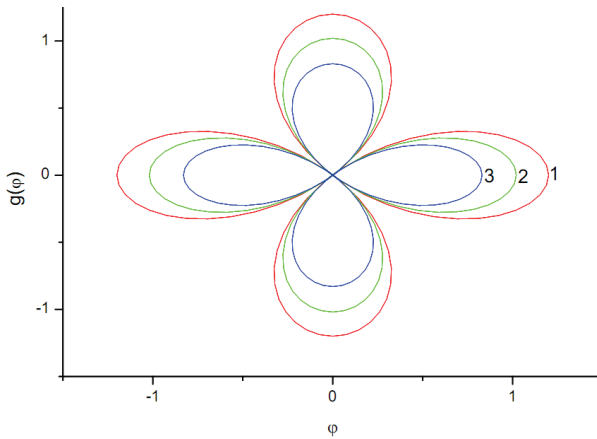


Fig. 1. (Color online) Angular part of the superconductivity gap.

### 3. Specific Heat Capacity of Organic Superconductors

The Bogolyubov–de Gennes equations (1) were solved together with Eq. (3) numerically by using our computer software. Then we found the specific heat capacity of some organic superconductors by formula (4). We determined numerical values of their parameters, which lead to a good agreement with experimental data on the heat capacity. Such parameters are the width of the superconductivity gap and two parameters related to the temperature dependence of the superconductivity gap.

We have done the computer calculations for  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br with the following parameters:  $\Delta(0) = 1.875 \times 10^{-3}$  eV;  $\delta = 1.86$  and  $c = 0.84$ . The results of calculations are shown in Fig. 2, where the theoretical results are drawn

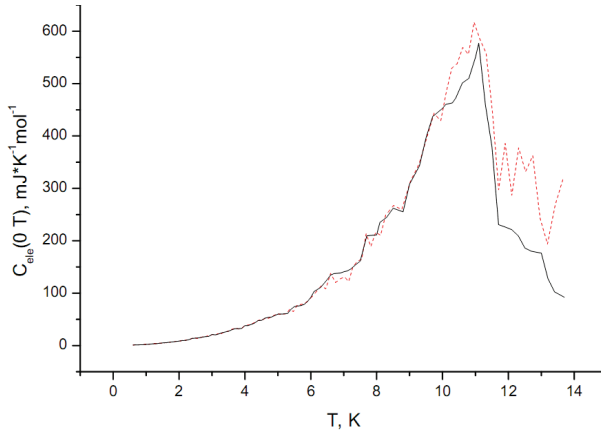


Fig. 2. (Color online) Specific heat capacity as a function of the temperature for the organic compound  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br for experiment (black line) and theory (red line).

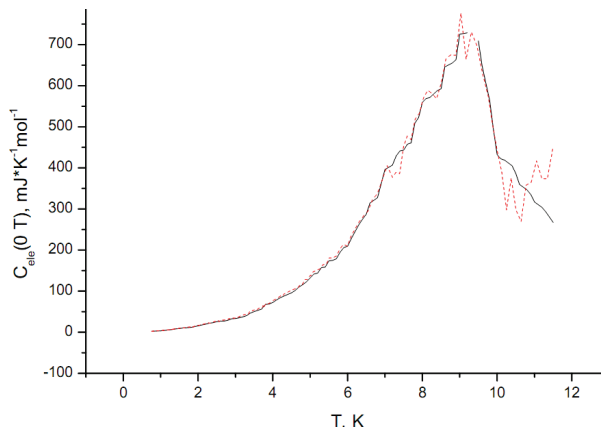


Fig. 3. (Color online) Specific heat capacity as a function of the temperature for the organic compound  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> for experiment (black line) and theory (red line).

as the red line, whereas the experimental data are given by the black curve. Thus, we see quite reasonable agreement of theory and experiment.

Figure 3 presents the results of calculations of the specific heat capacity for the superconductor  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> with the parameters  $\Delta(0) = 1.478 \times 10^{-3}$  eV;  $\delta = 1.75$  and  $c = 1.02$ . We observe again a good agreement with experimental data.

In Fig. 4, we present the results of calculations for the organic superconductor  $\kappa$ -(BEDT-TTF)<sub>2</sub>Ag(CN)<sub>2</sub>H<sub>2</sub>O and compare them with experimental data. The used parameters are as follows:  $\Delta(0) = 6.623 \times 10^{-4}$  eV;  $\delta = 1.45$  and  $c = 0.98$ .

Figure 5 shows the temperature dependences of the gap width for the three compounds of organic superconductors: curve 1  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br, curve 2  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> and curve 3  $\kappa$ -(BEDT-TTF)<sub>2</sub>Ag(CN)<sub>2</sub>H<sub>2</sub>O.

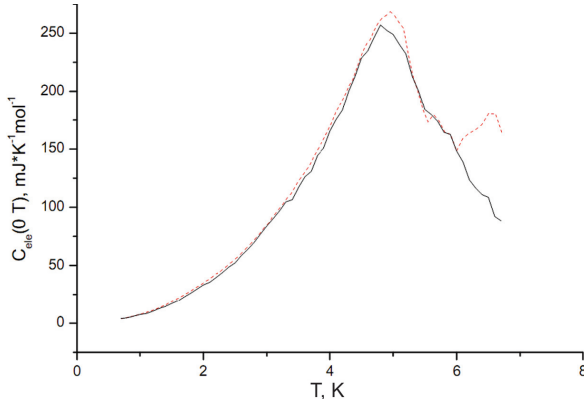


Fig. 4. (Color online) Specific heat capacity as a function of the temperature for the organic compound  $\kappa$ -(BEDT-TTF)<sub>2</sub>Ag(CN)<sub>2</sub>H<sub>2</sub>O for experiment (black line) and theory (red line).

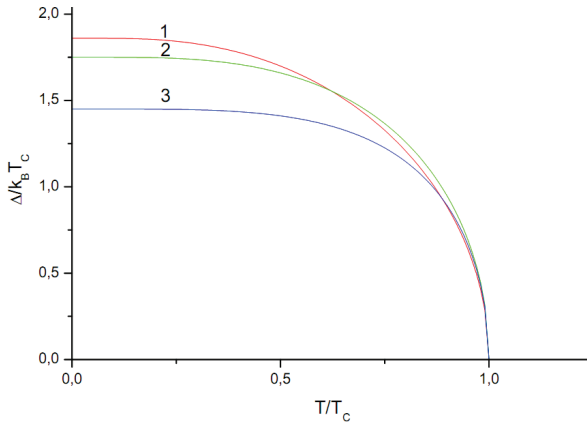


Fig. 5. (Color online) Calculated widths of the reduced superconductivity gap as a function of temperature.

## 4. Discussion

The problem of pairing symmetry is the problem of the pairing of charged fermions into states with the final orbital moment. As usual, both the standard pairing called the  $s$ -pairing and the nonstandard  $d$ -pairing are considered. They differ by the orbital moment of the pair: in the first and second cases, the moments are  $L = 0$  and  $L = 2$ , respectively.

Our calculations of the specific heat capacity of certain organic superconductors have confirmed that the superconductivity gap has the  $d$ -symmetry.

## 5. Conclusion

The problem of definition of a gap symmetry in organic superconductors is of significant importance. The analysis of the temperature dependence of the specific heat capacity is a powerful tool for examining the pairing symmetry. Although it does not detect the phase of the order parameter, this bulk probe is very sensitive to the gap structure on the Fermi surface. There are many experiments devoted to the investigation of the  $d$ -wave symmetry of the superconductivity gap.<sup>2-4,10</sup> The present thermodynamical calculations may be an additional test in the definition of the symmetry of gaps in organic superconductors.

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