ELSEVIER

Synthetic Metals 70 (1995) 911–912

SYNTHETIC METALS

STM Spectroscopy in Superconducting Phase of $(BEDT-TTF)_2Cu(NCS)_2$

K. Nomura, K. Nagao, K. Ichimura and N. Matsunaga

Department of Physics, Hokkaido University, Sapporo 060 Japan

Abstract

The superconducting phase of $(BEDT-TTF)_2Cu(NCS)_2$ was investigated with use of the scanning tunneling microscope (STM). The tunneling conductance was measured at the b–c surface of a single crystal. The differential conductance shows a clear superconducting gap structure below the transition temperature and its value is reduced to almost zero around zero bias voltage at 1.9 K. The conductance curve is not well fitted to the BCS one but suggests the gap anisotropy. However, the gap with line nodes, expected from the simple d-wave symmetry, is excluded. Possible models for the superconducting gap are as follows; (1) the gap with point nodes or (2) the anisotropic gap with a minimum value Δ_{min}~1 mev. It is understood that the superconducting gap is highly anisotropic in k–space.

1. INTRODUCTION

Since the superconducting transition temperature exceeding 10 K was realized in the organic conductor $(BEDT-TTF)_2Cu(NCS)_2$, a lot of investigations have been done in order to clarify the mechanism of the superconductivity. It is recognized that the quasi-two dimensional electronic band with relatively strong correlation plays the main role. Several exotic behaviors different from the conventional superconductivity have been reported. One of them is for the symmetry of pair wave function. The most investigated one is the temperature dependence of the magnetic field penetration depth. The T^2 dependence was reported by the earlier magnetization measurement [1]. The μSR measurement [2] has shown the T linear dependence in lower temperature range. These seem to support the gapless nature. On the other hand, the surface impedance measurement in the micro-wave range [3] has obtained the thermally activated type behavior fitted to the conventional BCS curve.

The tunneling spectroscopic measurement is the most direct method for the determination of the superconducting gap structure. However, fully reliable tunneling data have not been obtained yet, partly due to poor control of the tunneling barrier. Bando et al. have reported [4] the gap value from their STM spectroscopic measurement. However, they couldn't discuss the gap structure in detail, because their differential tunneling conductance was not reduced to zero at zero bias.

We have done the tunneling spectroscopic measurement in single crystal of $(BEDT-TTF)_2Cu(NCS)_2$ with use of the STM and observed a clear superconducting gap structure. In this article, we present the experimental results and discuss the superconducting gap symmetry in this material.

2. EXPERIMENTAL

Single crystals of $(BEDT-TTF)_2Cu(NCS)_2$ were grown electro-chemically. The superconducting transition temperature was determined from the resistive transition as 10 K. The detail of our low-temperature STM apparatus was described in our previous article [5]. A mechanically sharpened Pt wire was used as a tunneling tip. The b–c surface was mainly investigated. Because the cleavage of single crystal was not possible, we have tried to rinse the sample surface with ethanol or acetone in order to obtain a clean surface. However, the quality of tunneling spectra was not much improved by such surface treatments.

3. RESULTS AND DISCUSSION

In the STM spectroscopic measurement, we tried to obtain reliable tunneling spectra with varying the tip position and the tip distance from the sample surface and changing the surface treatment. However, we mostly obtained the V-shaped differential conductance dI/dV, which remained appreciable magnitude even at zero bias and didn't show any superconducting gap structure. In several runs, we could obtain the clear superconducting gap structure. In these cases, we could also obtain the temperature dependence, although we couldn't confirm the precise condition of tunneling barrier.

Typical tunneling conductance curve obtained at 1.9 K is shown in Fig.1. In the figure, the gap structure is clearly recognized. The height of outer peak of the gap is relatively small as compared with that of BCS curve. This peak structure was not fully reproducible but showed a slight change depending on the tip position or the tip distance. In some cases, the peak structure was more pronounced. However, we confirmed that the conductance curve is essentially the same at the inside region of the superconducting gap, as observed in the case of cuprous oxide superconductor [5]. This behavior is possibly explained by the energy dependence of the tunneling probability through the surface layer. Accordingly, we discuss only the functional shape in the low energy region, where the tunneling probability is considered to be almost constant and the differential tunneling conductance is proportional to the electronic density of states in

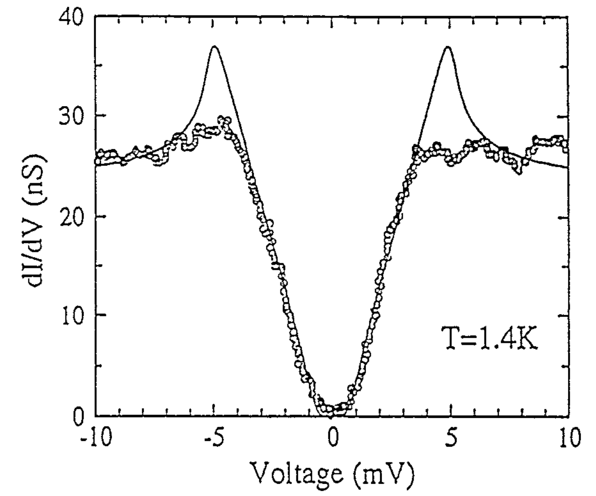

Figure 1 Differential tunneling conductance curve at 1.9 K. Solid line represents the fitting by the anisotropic gap model.

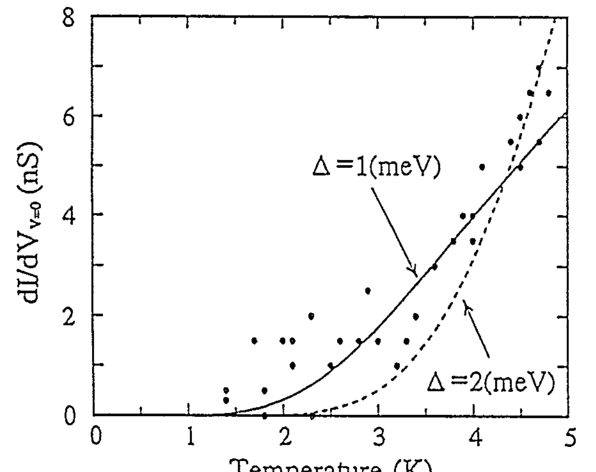

Figure 2 Temperature dependence of $dI/dV_{V=0}$. Solid and broken lines represent theoretical curves expected from the BCS with Δ=1 meV and Δ=2 meV, respectively.

the superconducting phase.

The differential conductance is reduced to almost zero around zero bias voltage in the low temperature, as in Fig. 1. However, it is apparent that the conductance curve cannot be fitted to the BCS curve, even if we take the broadening effect of each electronic level into account. It strongly suggests some anisotropic gap; the pair symmetry other than the s–wave. Simple theoretical candidate for the anisotropic gap is the d–wave symmetry with line nodes. The line nodes model gives the linear dependence of the electronic density of states to the energy in the low energy region. Such a energy dependence is quite different from the observed one. It looks rather quadratic on the bias voltage at first sight. If we introduce the broadening effect of one electron level, the quadratic dependence may be reproduced even for line nodes case. However, the calculated value at zero bias is raised appreciably even at 0 K and cannot explain the observed zero conductance. Simple d–wave symmetry is definitely excluded by the present result. The quadratic dependence naively suggests that the superconducting gap has nodes at point on the Fermi surface, although the exact mechanism giving point nodes is not clear in the quasi–two–dimensional band. It is understood that the gap vanishes at points if the gapless nature is correct.

As discussed above, the broadening effect of one electron level can bring about the quadratic dependence. In the case where the original gap is finite on the whole Fermi surface, the zero bias conductance remains zero at the low temperature even with including the level broadening. We show the fitting by the finite gap model, where the gap is assumed to vary from Δ_{min}=0.9 meV to Δ_{max}=5.2 meV on the direction of k–space as discussed for the cuprous oxide superconductor [5]. In the fitting curve, only the effect of finite temperature is taken into account. This model explains the observed result in the low voltage region satisfactorily. The slight discrepancy around zero bias is much improved, if we introduce the life time broadening effect.

In Fig. 2, we show the temperature dependence of zero bias conductance $dI/dV_{V=0}$ in order to discuss the low energy excitation in detail. This quantity is sensitive to the gap structure similarly to the magnetic field penetration depth λ. The origin of $dI/dV_{V=0}$ is absolute zero, while that of λ is determined only experimentally. This quantity has, accordingly, a great advantage for discussing the low energy excitation as compared with λ. We can again exclude the line nodes associated with the simple d–wave symmetry bringing about the T linear dependence. The curve may be roughly described by the T^2 dependence. This is consistent with the quadratic dependence of tunneling conductance in the low energy region. However, it is also possible to consider the result as the thermally activated type. In Fig. 2, we show curves expected from the BCS density of states. Better fitting is obtained for Δ=1 meV. This value is roughly equal to the minimum gap value Δ_{min}=0.9 meV obtained from the fitting of conductance curve. This is also consistent with the finite gap model discussed above.

As a result, two models are possible for understanding the present tunneling results. The obtained conductance curve and its temperature dependence are consistent with both models within experimental errors. It is understood that the superconducting gap in $(BEDT\text{–}TTF)_2Cu(NCS)_2$ is highly anisotropic and the gap value is reduced to 1 meV or less at some direction of the k–space. It needs further investigations in high quality sample to determine which is essential unambiguously.

REFERENCES

1. K. Kanoda, K. Akiba, K. Suzuki, T. Takahashi and G. Saito, Phys. Rev. Lett., 65 (1990) 1271.
2. L. P. Le, G. M. Luke, B. J. Sternlief, W. D. Wu and Y. J. Uemura, Phys. Rev. Lett., 68 (1992) 1923.
3. M. Dressel, S. Bruder and G. Grüner, Phys. Rev., B48 (1993) 9906.
4. H. Bando, S. Kashiwaya, H. Tokumoto, H. Anzai, N. Kinoshita and K. Kajimura, J. Vac. Sci. Technol., A8 (1990) 479.
5. K. Ichimura and K. Nomura, J. Phys. Soc, Japan, 62 (1993) 3661.