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POSITRON ANNIHILATION STUDIES OF ORGANIC SUPERCONDUCTIVITY

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ABSTRACT

The positron lifetimes of two organic superconductors, κ -(ET)₂Cu(NCS)₂ and κ -(ET)₂Cu[N(CN)₂]Br, are measured as a function of temperature across T_c . A drop of positron lifetime below T_c is observed. Positron-electron momentum densities are measured by using 2D-ACAR to search for the Fermi surface in κ -(ET)₂Cu[N(CN)₂]Br. Positron density distributions and positron-electron overlaps are calculated by using the orthogonalized linear combination atomic orbital (OLCAO) method to interpret the temperature dependence due to the local charge transfer which is inferred to relate to the superconducting transition. 2D-ACAR results in κ -(ET)₂Cu[N(CN)₂]Br are compared with theoretical band calculations based on a first-principles local density approximation. Importance of performing accurate band calculations for the interpretation of positron annihilation data is emphasized.

INTRODUCTION

The recent discovery of organic donor-molecule-based superconductors with T_c in excess of 10 K in the (BEDT-TTF)₂-X charge-transfer salts, where BEDT-TTF denotes bis(ethylenedithio)-tetrathiafulvalene (abbreviated as ET) and X is an inorganic anion, has opened a new area of research in superconductivity [1]. With X = Cu[N(CN)₂]Br⁻ and X = Cu[N(CN)₂]Cl⁻, for example, the transition temperatures (diamagnetic onset) are found to be 11.6 K (ambient pressure), and 12.8 K (0.3 kbar), respectively. Because of the structural similarities between these materials (Fig.1) and cuprate high- T_c superconductors, such as YBa₂Cu₃O₇, the understanding of the superconducting properties and mechanism in these organic systems may give further insight into the nature of high T_c materials.

EXPERIMENTS

Single crystals of κ -(ET)₂Cu(NCS)₂ compounds were synthesized [2] at Kyoto University. The crystals have disk-like shapes with typical dimensions of 2mm × 1mm × 0.2 mm. The largest face of the disk is parallel to the conducting planes (*b-c* planes). Single crystals of κ -(ET)₂Cu[N(CN)₂]Br compounds were synthesized [3] at Argonne National Lab. The size of the crystal used is 2.5mm × 2.0 mm × 0.4mm. The largest face of the disk is parallel to the conducting *a-c* planes. X-ray diffraction showed both of these two crystals to be single and κ phase. The superconducting transition onsets and widths of these two crystals were determined from magnetic susceptibility measurements to be 8.6 ± 0.2K and 10.5 ± 0.2K, respectively.

Lifetime spectra at various temperatures from 4K to 295K in these two crystals were measured. Both spectra were best fitted to two components with long-lived components of intensities only about 0.2% to 0.3% which were attributed to the o-Ps annihilation in the surfaces between crystals. Nearly 100% of the shorter lifetime indicates the high quality and nearly defect-free crystals, which are ideal for the search for the Fermi surfaces.

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Fig. 1. Crystal structures of:
(a) κ -(ET)₂Cu(NCS)₂ and
(b) κ -(ET)₂Cu[N(CN)₂]Br

(a) κ -ET₂Cu(NCS)₂ Structure

(b) κ -ET₂Cu[N(CN)₂]Br Structure

RESULTS

κ -(ET)₂Cu(NCS)₂

The short lifetime component (τ) with an intensity $\geq 99.7\%$ vs temperature at the range between 4 K and 294 K, and details around T_c are shown in Fig.2 (a) and (b). It is observed that: (1) τ undergoes a rapid decrease as T decreases below T_c , (2) τ increases monotonically but slowly with T above T_c , (3) the values of τ (between 343-372 ps) are long compared to other metals, but are about the same magnitude as that in C₆₀-based materials [4].

Fig. 2. Temperature dependence of lifetime in κ -(ET)₂Cu(NCS)₂: (a) 4-16K, (b) 4-295K [5].

The monotonic increase of τ above T_c can be understood as arising from an expansion of the crystal lattice volume as T increases. Since the positron lifetime is an integral of the positron and the electron densities [6], the magnitude of τ is roughly proportional to the cell volume of the crystal when the positron wavefunction effect is ignored [5].

The rapid decrease of τ below T_c is interpreted in the light of positron density distribution (PDD) calculation, which is calculated by solving the Schrodinger equation with the positron potential taken as a sum of the potential due to electron and ions from the OLCAO method and the correlation potential in the local density approximation [6]. The calculated PDD in κ -(ET)₂Cu(NCS)₂ is plotted in Fig.3 for three planes along the a -axis. The maxima of the PDDs are all in the regions between atoms. This is an expected result since the positron is repelled by the ion cores in the lattice in its Bloch state. The integrated positron density and positron-electron overlap distribution were calculated along the a -axis and the large value of the positron-electron integral near the Cu(NCS)₂ layers shows that most annihilation is due to these regions [5].

The anionic $\text{Cu}(\text{NCS})_2$ regions are insulating layers (110.3°) which intercent the a -axis with $a=16.25\text{\AA}$. The conducting carriers are believed to be the holes from the π -electrons of cationic $(\text{ET})_2$ along the b - c planes. A decrease of τ at the superconducting transition implies an increase of the local electron density near the $\text{Cu}(\text{NCS})_2$ layers. In order to maintain total charge conservation, a local-charge transfer should occur during the superconducting transition. $(\text{ET})_2$ layers are the best candidates to donate charges and result in the reduced local charge density around these regions. On the other hand, a net increase of electron density near the $\text{Cu}(\text{NCS})_2$ layers, where the positron is highly populated, occurs at the onset of superconductivity. This suggested interpretation is consistent with the experimental fact that this kind of lifetime- T_c dependence is only observed in the systems where the conducting carriers are holes [1,2]. Similar changes of positron lifetime and local charge transfer have been observed in cuprate high temperature superconductors [7], but not in conventional BCS superconductors.

Fig. 3. Positron density distribution along a -axis in κ -(ET) $_2\text{Cu}(\text{NCS})_2$ [5].

κ -(ET) $_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$

The analyzed lifetime results are : $\tau_1 = 310 - 344$ ps, $I_1 = 99.7\%$, $\tau_2 = 1560 \pm 50$ ps, which are very similar to those in κ -(ET) $_2\text{Cu}(\text{NCS})_2$. τ_1 is consistent with the theoretical calculated Bloch-state lifetime (329 ps). A drop of lifetime below T_c similar to that in κ -(ET) $_2\text{Cu}(\text{NCS})_2$ is observed. The result of nearly 100% single positron-lifetime component verifies the high quality of the crystal and its suitability for the 2D-ACAR experiment.

The momentum-density experiment was performed with use of a 2D-ACAR spectrometer [8]. The 2D-ACAR spectra were accumulated on a 256×256 matrix of 0.143×0.143 mrad cells. The instrument angular resolution was 0.720 mrad with the crystal at 300K under a vacuum of 10^{-4} Torr. The 2D-ACAR results were performed at room temperature under vacuum. The total count of 2D-ACAR spectrum was 6×10^7 .

(a)

(b)

Fig. 4. (a) Calculated Fermi surface of κ -(ET) $_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ [10]. (b) Reduced momentum density of the LCW folded 2D-ACAR spectrum [8].

Generation of the LCW density [9] from the measured momentum spectrum disclosed a density with a mean amplitude of $\approx 10^6$ counts per bin and an overall amplitude variation of $\approx 0.3\%$, or little more than three calculated standard deviations (3σ). In light of that, the data were smoothed with a 5-point by 5-point kernel to improve the signal-to-noise ratio. In the resulting smoothed distribution (Fig.4(a)), there is an effective degradation in resolution (to 0.90 mrad FWHM) but the total amplitude variation is improved to 6σ . It is obvious that there is a strong resemblance in the topological features of the contours between this data and the calculated Fermi surface, based on the first-principles calculation of the OLCAO method [10]. The major difference is at the BZ edge along the U(M)-Z direction, where the calculation shows an open channel and the experimental data somehow show unexpected anomalous features. We believe this is due to insufficient positron-electron annihilation data at this particular region of the BZ in the 2D-ACAR method. The exact mapping of the Fermi surface by using the 2D-ACAR method is in progress.

SUMMARY

The existing results of positron lifetime, 2D-ACAR, and first-principles calculations show a promising future for use of PAS to investigate the electronic structure, the Fermi surface, and superconductivity in organic superconductors. The sensitive response of the positron lifetime across T_c in organic superconductors shows that the positron is particularly sensing the electrons responsible for superconducting transitions. Significant scientific information from lifetime experiments can be obtained only when accurate positron and electron densities are available. This can be achieved only by a close collaboration between experimentists and theorists. As for as the Fermi surface studies, accurate band calculations are even more crucial for the positron research. Popular theoretical approaches by atomic approximation [11] are found to be inadequate for complex systems. Not only are these crude calculations incorrect in electron-positron densities, but they may also be misleading in terms of the experimental results obtained from the 2D-ACAR method. Only accurate band approaches can make scientific significance from PAS results in organic and molecular systems.

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