TEMPERATURE DEPENDENCE OF THE CHEMICAL POTENTIAL OF HIGH–Tc SUPERCONDUCTORS

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We discuss the behaviour near T_c of the chemical potential for superconductors consisting of a dilute gas of interacting fermions, using a BCS mean field approach. When the gap parameter Δ becomes of the order of magnitude of the Fermi energy E_F, the chemical potential is influenced by the opening of a gap. This effect is shown to be of the order of several tenths of a millielectronvolt for cuprate oxide superconductors. We show that it is possible to determine this anomaly as a function of temperature by determining the work function, and describe our experimental set up and some preliminary results.

1. INTRODUCTION

In research on high-T superconductors little work has been done so far to study the temperature dependence of the chemical potential. This can however provide insight into the nature of the pairing in these ceramic materials.

When dealing with a ground state of large overlapping Cooper pairs the exclusion principle will be dominant and no variation in the chemical potential will occur near T_c (1,2). On the other hand when we consider a dilute gas of particles interacting on a small length scale, we expect that the behaviour of the pairs will resemble that of point bosons. When the gap opens, the chemical potential will change in order to conserve the number of particles.

2. THEORY

For the calculation of the chemical potential we will start with the coupled BCS equations,

$$2 \Delta_k = \sum_{kq} V_{kq} \frac{1 - 2f(\beta E_q)}{E_q} \Delta_q$$

$$N = \sum_k \left(1 - \frac{\varepsilon_k}{E_k} + 2\frac{\varepsilon_k}{E_k} f(\beta E_k)\right),$$

where E_k are the quasiparticle energies en ε_k are the single electron energies relative to the Fermi level. We briefly give the results here, a complete discussion was given in (1).

Following BCS we assume a retarded attractive potential $-V$ in a region $\pm D$ around E_F. The nature of the attractive interaction is unimportant for our discussion. In the dilute limit the cutoff energy D will be larger than the chemical potential relative to the bottom of the band μ, so the lower cutoff will be the bottom of the band. The interaction interval thus becomes $[-\mu, D]$.

Solving μ from the number equation at T=0 gives

$$\mu = \tilde{\mu}_n - \frac{E_a}{2} \quad , \quad E_a = \frac{\Delta^2}{2\tilde{\mu}_n} \quad ,$$

with $\tilde{\mu}_n = \mu_n + \frac{1}{2}(\sqrt{D^2 + \Delta^2} - D)$ reducing to μ_n, the chemical potential in the normal state, for D much larger than the energy gap Δ. We see that the chemical potential is changed by half the binding energy in the two-particle problem, E_a, a result also found by Randeria et al.(3).

Fig. 1 shows the results of a numerical solution of the full-temperature dependent coupled gap equations for different values of the normal state chemical potential at zero temperature μ_n. The interaction parameters were chosen such as to give a critical temperature in the range of the high-T_c superconductors. We see that with these parameters the shift in the chemical potential is of the order of several tenths of a millielectronvolt. Note that this kink-like behaviour is not found by Schmitt-Rink and Varma (4).
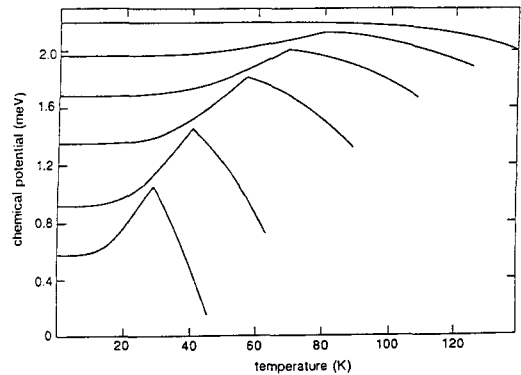

FIGURE 1
Temperature dependence of the chemical potential for a superconductor with exp(–2/nV)=0.0183, where V is a retarded potential with a cutoff energy of 0.05 eV. The normal state chemical potential at zero temperature μ_n is from top to bottom:0.05, 0.04, 0.03, 0.02, 0.01 and 0.005 eV.

Their results are probably valid for temperatures sufficiently larger than the BCS T_c, which may explain the difference.

3. MEASUREMENT TECHNIQUE

One way to measure changes in the chemical potential of a conductor is to measure its workfunction. In principle the workfunction is the sum of two components: the chemical potential of the material and the potential barrier at the surface due to the surface electronic structure (5). In practice, there is an additional contribution caused by the adsorption of gas molecules on the metal surface. As we are only interested in changes of the chemical potential in dependence of temperature, the experimental conditions have to be chosen such that the other components of the workfunction remain constant. In practice this means measuring in ultra high vacuum. We suppose that the contribution of the surface structure shows no anomaly near T_c, which is a reasonable assumption if there is no structural phase transition in that temperature range.

From fig.1 it is clear that the measurement method should have a resolution well below a millivolt. This can be achieved with the Kelvin probe or Contact Potential Difference method. Here the sample surface and a reference electrode form a capacitor with capacitance C. The charge on each electrode will be C ΔW, where ΔW is the difference in the workfunctions of sample and reference surface. When C is changed sinusoidally, e.g. by vibrating one of the electrodes, an ac current is generated in the wire connecting the sample and the reference electrode. If an external dc backing voltage V_b is included in series in the circuit and adjusted until the ac current is zero, then in this condition ΔW must be equal in magnitude and opposite in polarity to V_b (5,6).

In practice the main problems with the Kelvin probe method are noise, stray capacitances and the cleanliness of the reference electrode (6). Especially the exact nature of the reference electrode surface puts a severe limitation on this method.

4. RESULTS

The sample is an E-beam evaporated thin film (thickness: 3000 Å) of YBaCuO on a [001] oriented SrTiO substrate. X-ray diffraction showed mainly [001] orientation of the evaporated layer. From resistivity measurements $T_{c,0}$ was found to be 88 K.

The samples were mounted onto a cold finger with the Au-reference electrode approximately 1 mm above the sample surface. The reference electrode was attached to a vibrating reed driven by a piezoelectric element (7). The whole system was put in an ion-pumped vacuum system. After bakeout, the pressure was in the 10^{-9} mbar range. With the cold finger we were able to cool the sample below 20 K.

Fig.2 shows the result of a workfunction measurement on the YBaCuO sample. It was measured during heating of the sample.

Between 50 and 75 K an increase of the pressure was seen. Therefore we believe that the increase of the workfunction in this temperature range is due to desorption of gas from the sample surface. Above 75 K the pressure was essentially constant. At about 100 K a clear kink is visible, which might be related to the disappearance of
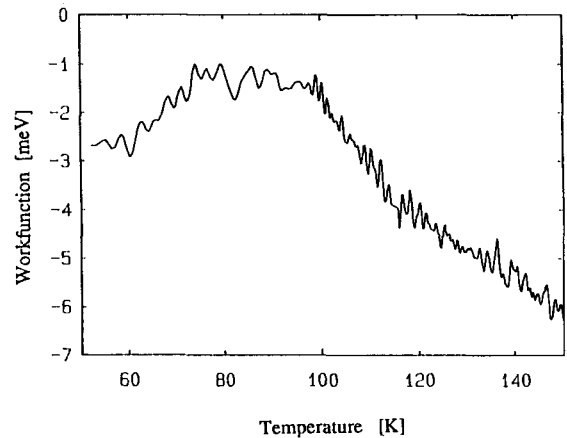

FIGURE 2
The workfunction of YBaCuO as a function of temperature.

superconductivity. During this experiment the thermal contact between the sample and the Pt-100 thermometer was bad, which may explain the difference between $T_{c,0}$ and the temperature of the kink.

5. CONCLUSIONS

We have measured a clear kink in the temperature dependence of the workfunction of the high Tc superconductor YBaCuO. This anomaly is in reasonable agreement with what we expect from theoretical considerations based on the low density of charge carriers and the low value of the chemical potential compared to the cutoff energy of the high-T_c superconductor. Further experiments will have to confirm this preliminary result.

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