CORRELATIONS BETWEEN T_c AND n_s/m^* (CARRIER DENSITY / EFFECTIVE MASS) IN HIGH-T_c AND ORGANIC SUPERCONDUCTORS

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We update our muon spin relaxation studies of the magnetic field penetration depth which show the correlations between T_c and the relaxation rate $\sigma \propto n_s/m^*$ (carrier density/effective mass) of hole-doped high-T_c cuprate superconductors $(La_{2-x}Sr_x)CuO_4$, $YBa_2Cu_3O_y$, $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$, and other double and triple layer systems. These studies are extended to the organic superconductor $(BEDT-TTF)_2Cu(NCS)_2$.

1. Introduction

In the transverse-field μSR measurements on type-II superconductors, one can determine the magnetic field penetration depth λ, which is related to the superconducting carrier density n_s divided by the effective mass m^*. In general, a larger carrier density n_s and a lighter effective mass m^* produces a more effective screening of the external field, and thus resulting in a shorter penetration depth λ. In the clean limit where the coherence length ξ is much shorter than the mean free path l, which is the case for most of the hole-doped high-T_c superconductors, the muon spin relaxation rate is related to n_s/m^* by a simple relation $\sigma \propto 1/\lambda^2 \propto n_s/m^*$. We have performed extensive μSR measurements [1–4] of the penetration depth in many different compounds of cuprate high-T_c superconductors, in order to study the relation between T_c and $\sigma \propto n_s/m^*$. In this paper, we update this research including the data on ceramic specimens of $(La_{2-x}Sr_x)CuO_4$, $YBa_2Cu_3O_y$, $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$, and other double and triple layer cuprate superconductors. We have found remarkable correlations between

T_c and $\sigma(T\to 0)$, the implications of which will be discussed in terms of some theoretical models for high-T_c superconductivity. We have also performed μSR measurements of the penetration depth in an organic superconductor (BEDT−TTF)$_2$Cu(NCS)$_2$.The results of this organic system are compared with those of the cuprate high-T_c systems.

2. Relations between σ, λ, n_s, m^*, ξ and l

When an external magnetic field $H_{ext}(H_{c_1} < H_{ext} < H_{c_2})$ is applied to type-II superconductors, it penetrates into the specimen by forming a lattice of flux vortices. Pincus et al. [5] showed that the width ΔH of the local field distribution $P(H)$ in the vortex state is nearly independent of H_{ext} with $\Delta H \propto 1/\lambda^2$ over a wide range of H_{ext}. For simplicity, we assume a Gaussian distribution of the local fields, which corresponds to the dephasing of the muon spin precession with a Gaussian envelope $\exp(-\sigma^2 t^2/2)$. The penetration depth λ can be determined through the relation

$$\sigma \propto \Delta H \propto 1/\lambda^2. \tag{1}$$

For unoriented ceramic specimens, λ represents an angular average over the anisotropic penetration depths, $\lambda_{\parallel}$ for c-axis $\parallel H_{ext}$ and $\lambda_{\perp}$ for $c \perp H_{ext}$. In highly anisotropic cuprate and organic superconductors where $\lambda_{\parallel} \ll \lambda_{\perp}$, ΔH is determined predominantly by the in-plane penetration depth $\lambda_{\parallel}$. In the derivation of the absolute values of λ, different modelling for $P(H)$ and the angular average could result in systematic uncertainty of up to 30%. The statistical accuracy for the relative values (i.e., temperature and material dependences) of λ is, however, much better than $\pm 5\%$ error.

In general, the measured penetration depth λ is related with n_s, m^*, ξ and l as

$$1/\lambda^2 = \frac{4\pi n_s e^2}{m^* c^2} \times \frac{1}{1+\xi/l}, \tag{2}$$

where e is the elementary charge and c the light velocity. The coherence lengths ξ of cuprate high-T_c superconductors are very short; typically about 10 ~ 20 Å within the CuO_2 planes. On the other hand, the normal state resistivity, measured [6] on single crystals of $YBa_2Cu_3O_y$ with $y = 6.5 \sim 7.0$, indicates that the mean free path l of charge carriers on the CuO_2 plane is longer than 100 Å at temperatures near T_c; the strong temperature dependence of the resistivity suggests that l is likely to be longer than this value at low tempratures below T_c. The resistivity measurements provide the lower limit for the values of mean free path; the real values in the material may even be longer. An independent light scattering study [7] also indicates l ($T = 100$ K) = 160 Å in $YBa_2Cu_3O_7$. In such a "clean limit" ($\xi/l \ll 1$) situation, the correction terms ξ/l in eq. (2) becomes negligible, and one then expects $\sigma \propto \Delta H \propto 1/\lambda^2 \propto n_s/m^*$.

3. Universal Correlations

We have performed TF-μSR measurements on more than 30 different specimens of cuprate high-T_c superconductors [1–4]. Fig. 1 shows a plot of T_c versus $\sigma(T \to 0) \propto n_s/m^*$, both determined by μSR on these systems. With increasing carrier density, T_c initially increases, then saturates, and finally is suppressed in the heavily doped region. This tendency can be seen universally [2] in the single layer $La_{2-x}Sr_xCuO_4$ (214), double layer $YBa_2Cu_3O_y$ (123), as well as the triple layer $Bi_2Sr_2Ca_2Cu_3O_{10}$ (2223) and similar systems. Moreover, the initial increase of T_c with increasing n_s/m^* follows a straight line shared by the 214, 123, and 2223 systems.

Although it is impossible to separate the effect of n_s from that of m^* in the μSR measurement alone, it is quite likely that the results in fig. 1 predominantly reflect the differences of n_s among various specimens. For a typical value of $m^* = 5\ m_e$, $\sigma = 1\ \mu\text{sec}^{-1}$ corresponds to a carrier density of $n_s \sim 2 \times 10^{21}\ \text{cm}^{-3}$. Therefore, the results in fig. 1 are generally consistent with the estimates of the carrier density based on the stoichiometry and valency. Indeed, the results consistent with fig. 1 are obtained in the measurements of Hall coefficient R_H (ref. (8)) and plasma frequency ω_p (ref. (9)) which probe the normal state carrier density n_n as $1/R_H \propto n_n$ and $\omega_p^2 \propto n_n/m^*$. The μSR measurement, however, has an advantage since it reflects the actual superconducting carrier density.

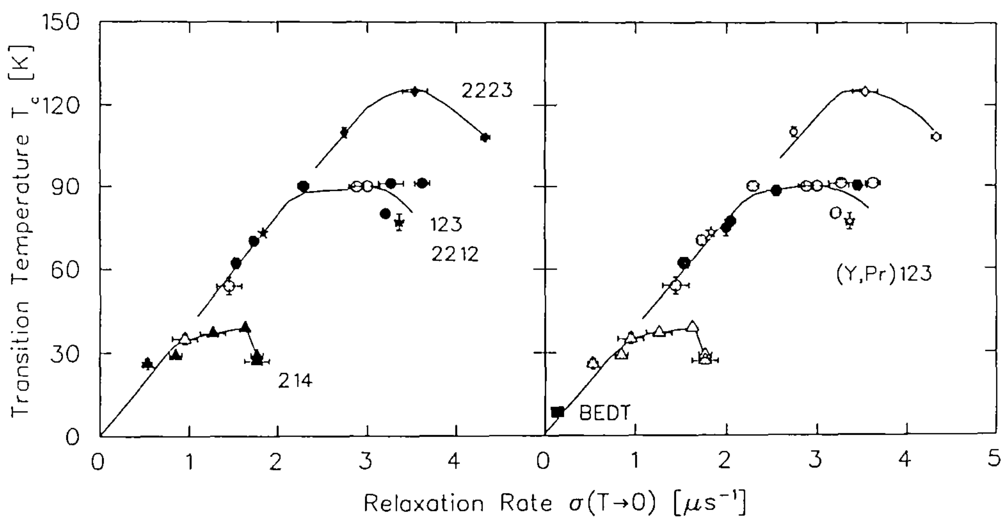

Fig. 1. The superconducting transition temperature T_c of various high-T_c superconductors plotted versus the low temperature values of the muon spin relaxation rate $\sigma(T \to 0)$. Both T_c and σ have been determined by μSR measurements. In the "clean limit" $\xi/l \ll 1$, $\sigma \propto 1/\lambda^2 \propto n_s/m^*$. The left figure (a) represents points from fig. 2 of ref. [2] (see the figure caption in ref. [2] for details), where the points for the 123 system are obtained with the oxygen depleted specimens $YBa_2Cu_3O_y$. The closed circles in the right figure (b) represent $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ with $x = 0.3$ to 0.05 (ref. [4]), and the closed square in (b) near the origin represents $(BEDT-TTF)_2Cu(NCS)_2$.

In the plot of T_c versus oxygen concentration y of the $YBa_2Cu_3O_y$ system, there is a "plateau" at $T_c = 60$ K. This has led some authors [10] to speculate that the 123 system with $T_c = 60$ K has some special "electronic phase". In a plot of T_c versus *measured* superconducting carrier density, such as fig. 1, however, no anomaly is present at $T_c = 60$ K. This is because the number of carriers on the CuO_2 plane remains nearly unchanged with increasing y in the "60 K plateau" region of $6.6 < y < 6.75$, as seen by μSR [2] and Hall effect [11] measurements. The extra holes with increasing y in this region are located therefore in some other part of the crystal. Thus, T_c increases smoothly as a function of the real carrier density n_s on the CuO_2 plane. This demonstrates that the $T_c = 60$ K plateau is merely an artifact of the crystal chemistry.

We have confirmed a further aspect of this by measuring $\sigma(T \to 0)$ for several specimens of $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ (ref. [4]). In the Pr doped 123 system, the carrier density is changed by the substitution of Pr^{4+} for Y^{3+}, avoiding complications from the crystallographic ordering of oxygen. As shown in fig. 1(b), the μSR results on the Pr doped 123 system give points in the T_c versus σ plot which agree very well with those of oxygen depleted 123 system. This is a further evidence that the transition temperature is determined by the carrier density in the CuO_2 plane, being insensitive to the method by which n_s is controlled. The good agreement of the results from oxygen depleted 123 and Pr substituted 123 systems further demonstrates that the results in fig. 1 reflect intrinsic properties of the cuprate superconductors. If the specimens were in the "dirty limit" with short mean free paths which are sensitive to defects and/or impurities in the material, one could not have expected such a good agreement for the two series of 123 systems. We should also note here that the carrier density n_s can be regarded as either the 3-dimensional or 2-dimensional density. Since the average distance between the CuO_2 planes is 6 ± 1 Å for all the different systems shown in fig. 1, they share approximately the same conversion factor between the 2-d and 3-d densities.

4. Implications

We have to wait for further theoretical development to fully understand the underlying mechanism which would give the results in fig. 1. We can, however, note the following points:

(1) The BCS theory gives the transition temperature as $T_c = \hbar\omega_B \exp(-1/VN(0))$ in the weak coupling limit, where $\hbar\omega_B$ is the energy scale of the boson which mediates the pairing (for conventional superconductors, it is the Debye frequency) and $N(0)$ the density of states at the Fermi level. The assumption here is that the Fermi energy ϵ_F is much larger than $\hbar\omega_B$. In the above formula for T_c, we can not expect a large dependence of T_c on the carrier density, since $\hbar\omega_B$ does not depend on n_s, and $N(0)$ in the 2-d noninteracting

electron system is constant. Therefore, fig. 1 encourages the development of theories different from the weak-coupling BCS theory with phonons as the mediating bosons.

(2) The linear relation between T_c and n_s/m^* can be expected [12] if $\hbar\omega_B$ is larger than ϵ_F. In this case, the pre-exponential factor of the above equation of T_c will be ϵ_F instead of $\hbar\omega_D$: for a 2-d electron gas ϵ_F is proportional to n_s/m^*.

(3) The linear relation between T_c and n_s/m^* can also be expected in theories based on a Bose-Einstein condensation [13]. The short coherence length of high-T_c superconductors motivates the development of this type of theory. Althogh the B-E condensation does not occur in 2-dimensional systems, slight three dimensional features could lead to a reasonable values of T_c comparable to those of the existing systems, as discussed by Lee and Friedberg [13].

(4) The relation $T_c \propto n_s/m^*$ can also be explained by "anyon" theory [14].

(5) The saturation and suppression of T_c in the heavily doped region has been predicted by theories based on spin frustration due to holes on oxygen sites, such as proposed by Aharony et al. [15].

5. Organic superconductor

Recently, we have extended this study to the organic superconductor (BEDT − TTF)$_2$Cu(NCS)$_2$.This system has the highest T_c (10.8 K in zero-field) among the organic superconductors [16]. The transport and H_{c_2} measurements [16] indicate highly 2-dimensional electronic properties and a low carrier density, as in the case in the high-T_c systems. Fig. 2 shows our current data on the temperature dependence of the muon spin relaxation rate σ measured with single crystal specimens with a transverse external field $H_{ext} = 3.1$ kG applied perpendicular to the conducting plane (the b-c plane). It should be noted that T_c is reduced to about 8 K in this field. These data are consistent with independent μSR work on the same material [17]. At the moment, we do not have enough statistical accuracy to distinguish the symmetry of superconducting pairing clearly (more data in the low temperature region are required).

After correction for the background relaxation contributions, the effect of the penetration depth at $T \to 0$ is found to be $\sigma \sim 0.12$ μsec^{-1}, which corresponds to a ground state penetration depth of $\lambda \sim 8000$ Å and $n_s/m^* = 4.6 \times 10^{19}\,\mathrm{cm}^{-3}/m_e$ in the clean limit. In the case of (BEDT − TTF)$_2$Cu(NCS)$_2$, if one carrier exists per molecule, each of which has a very large volume (845 Å^3 per molecule), the nominal carrier density n becomes $n = 1.2 \times 10^{21}\,\mathrm{cm}^{-3}$. Thus the observed small relaxation rate (long penetration depth) can be understood to result partly from the low carrier density due to the molecular size. The cyclotron mass m_c inferred from the Shubnikov-de Haas measurement [18] is about 3.5 m_e. Then the observed relaxation rate σ is about an order of magnitude smaller than the value expected from the nominal value n/m_c in the clean limit. Possible explanations

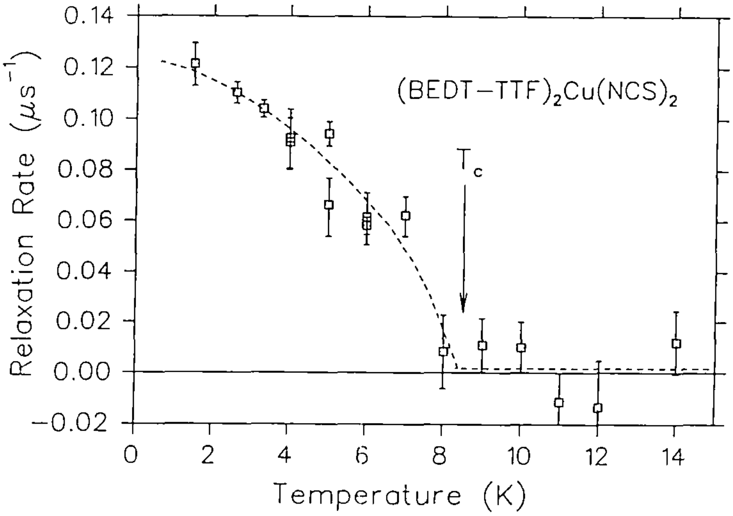

Fig. 2. Temperature dependence of the muon spin relaxation rate σ observed in single crystal specimens of the organic superconductor (BEDT − TTF)$_2$Cu(NCS)$_2$ with the external field H_{ext} = 3.1 kG applied perpendicular to the conductive $b-c$ plane. The low temperature relaxation rate (σ = 0.12 μsec^{-1} after correction for background relaxation) corresponds to a penetration depth of $\lambda \sim 8000$ Å. The broken line is a guide to the eye.

for this difference include: (a) a superconducting carrier density n_s smaller than n; (b) an effective mass m^* larger than m_e; (c) the correction term ξ/l in eq. 2 playing a role, i.e., deviation from the clean limit; or a combination of these.

It is also interesting to note that the results of σ and T_c for this organic system (BEDT − TTF)$_2$Cu(NCS)$_2$ give a point on the σ versus T_c plot of fig. 1 near the straight line shared by the cuprate high-T_c superconductors. If deviation from the clean limit condition is not very much in the organic system, then the point for the BEDT system in fig. 1 is directly comparable to those from cuprate systems, and the "universal correlation" can be extended even to the organic system. Further detailed μSR measurements on various organic superconductors are now underway.

Note added

Shubnikov-de Haas [18] and dc resistivity [16] measurements of (BEDT − TTF)$_2$Cu(NCS)$_2$ infer that the mean free path l of this system is longer than ~ 200 Å. The coherence length within the conductive b-c plane is ξ_{bc} ($T \to 0$) ~ 70 Å, indicating that this organic superconductor is close to the clean limit. Thus fig. 1 suggests that the correlation between T_c and n_s/m^* can be extended to the organic system. Assuming $\xi/l \ll 1$, we obtain the carrier density $n_s = 1.6 \times 10^{20}/cm^3$ for $m^* = 3.5\ m_e$ in (BEDT − TTF)$_2$Cu(NCS)$_2$ from the μSR results.

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