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Correlations between Mössbauer isomer shift and magnetic susceptibility in the high-T_c superconductor $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$

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Abstract. We find that there is a shift in the Mössbauer spectra which is proportional to the susceptibility of the system. The shift is calculated using the BCS value of the susceptibility. The predicted shift is compared with the experimental measurements of the Mössbauer line shift of ^{57}Fe in $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$ and found to be in reasonable agreement for $2\Delta/k_BT_c \simeq 3.6$ which is an adjustable parameter. This value of the ratio of the gap to the transition temperature is in reasonable agreement with the value of 3.52 predicted by the BCS theory.

In this paper, we report that there is a shift in the Mössbauer spectra which is proportional to the susceptibility. We calculate the susceptibility of a BCS superconductor which we use to predict the Mössbauer line shift in the superconducting state below the transition temperature. The calculated value of the shift is compared with the experimentally measured shift of the Mössbauer spectrum of ^{57}Fe in $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$. This comparison gives a value of $2\Delta/k_BT_c \simeq 3.6$ which is in reasonable agreement with the value of 3.52 predicted from the BCS theory. As the temperature dependence of the isomer shift (IS) is similar to that of the susceptibility it determines the transition temperature of the superconductor.

In velocity units the IS of the Mössbauer line is given by

$$\delta E = \tfrac{2}{5}\pi Ze^2R^2|\psi(0)|^2 c/E_\gamma \tag{1}$$

where c is the velocity of light and E_γ is the energy of the γ-rays. The factor c/E_γ converts the energy units into velocity units. R is the radius of the nucleus and $\psi(0)$ is the electronic wavefunction evaluated at the site of the nucleus.

If we apply an external magnetic field H, then the magnetic field inside the sample due to induction B_{in} is given by

$$B_{in} = \frac{4\pi M}{V} + H \tag{2}$$

where M/V is the magnetization per unit volume. We define the susceptibility as $\chi = M/VH$ in dimensionless units so that

$$\frac{B_{in}}{H} = 4\pi\chi + 1. \tag{3}$$

In the case of superconductors, $B_{in} = 0$, which is called the Meissner effect so that

$$\chi = -\frac{1}{4\pi} = -0.0795. \tag{4}$$

As the temperature approaches zero, the susceptibility of a superconductor approaches the value of −0.0795. By analogy with the paramagnetic shift [1] we use the susceptibility χa_0^{-3} instead of $|\psi(0)|^2$ to predict a new shift which is about

$$\frac{\chi a_0^{-3}}{|\psi(0)|^2} = 7.95\% \tag{5}$$

at zero temperature and vanishes at the transition temperature. Since the calculation of $|\psi(0)|^2$ *with spin–orbit interaction in a magnetic superconductor is not available, we observe* that the temperature dependence of $\chi(T)$ is the same as that of the IS. The advantage of using the diamagnetic susceptibility over the atomic susceptibility is that the superconducting state is a coherent state which is represented by the susceptibility slightly better than by the single-atom property $|\psi(0)|^2$, even in high-temperature superconductors where the coherence length is only tens of Ångströms. Thus the effect of the entire lattice is taken into account to describe the line shift. The estimate of the shift is affected by the difference between the susceptibilities of the absorber and the emitter. If one of these is kept at a constant temperature, then the susceptibility-dependent new shift can be detected by the temperature dependence of the susceptibility $\chi(T)$. The susceptibility-dependent shift is then given by

$$\delta E_\chi = \tfrac{2}{5}\pi Z e^2 R^2 a_0^{-3} \chi(T) \tag{6}$$

in energy units and

$$\delta E_\chi = \frac{2\pi Z e^2 R^2 c a_0^{-3} \chi(T)}{5 E_\gamma} \tag{7}$$

in velocity units such that $\delta E_\chi/\delta E \geqslant 0.08$. The shift (6) requires knowledge of the susceptibility. It is predicted that the measured line shift is linearly proportional to the measured susceptibility. It is also clear that the temperature dependence of the line shift is the same as that of the susceptibility.

In figure 1 we show the IS of ^{57}Fe in $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$ relative to Pd as a function of susceptibility which is linear as predicted. For this purpose we have taken the experimental measurements from the work of Wu *et al* [2]. In $YBa_2Cu_4O_8$ the Fe ions occupy four different sites and the data relate to only one of those sites, the square-pyramidal planar site. We have used the IS for the sample containing 2% Fe. Therefore, the susceptibility is also taken for the same sample. We have not used the susceptibility of the Fe-free samples. The s conduction electrons are scattered by the d electrons of the magnetic atoms, Fe in the present case, owing to the s–d exchange interaction, so that the susceptibility of Fe-containing samples is not the same as that of Fe-free samples. The transition temperature of the sample with 2% Fe is 62 K while that of the Fe-free sample is about 80 K. The effect of Fe is to reduce the attractive interaction of scattering electrons by its magnetic moment. The predicted linearity between the IS and the susceptibility is thus well demonstrated.

We *need not use the experimental value of the susceptibility to prove (6). Instead of the* experimental value, we can compute $\chi(T)$ from the BCS theory and substitute the calculated value in (7) to find the IS. The susceptibility of a superconductor is given by the BCS [3] theory with summation to all orders as

$$\chi(q,\omega) = \frac{\chi_0(q,\omega)}{[1 - \bar{U}_{\chi_\parallel}(q,\omega)]} \tag{8}$$

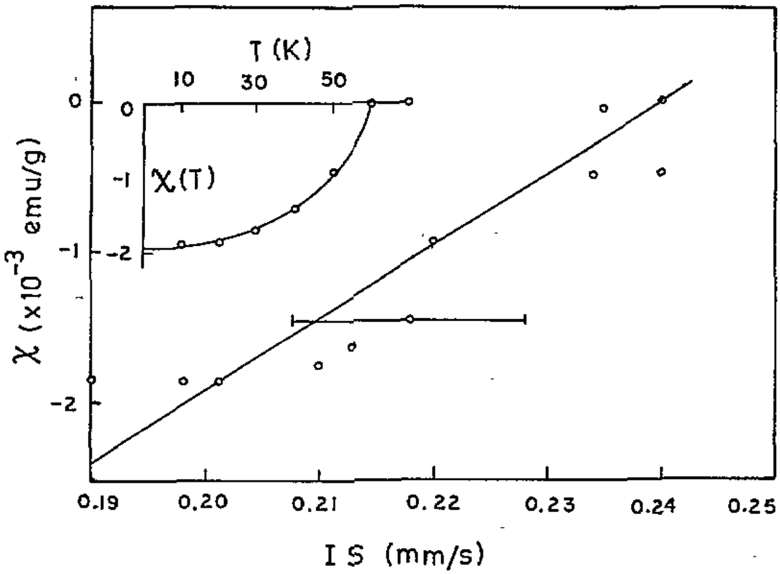

Figure 1. A plot of the susceptibility as a function of the IS for $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$ which is found to be linear. The inset shows the susceptibility as a function of temperature showing superconducting behaviour. The experimental values of $\chi(T)$ and IS (T) are taken from [2].

where $\bar{U}$ is the effective strength of the interaction [4]. The irreducible susceptibility is given by

$$\chi_0^{\mathrm{BCS}}(q,\omega) = \frac{1}{N}\sum_p \left(\xi_0 \frac{f(E_{p+q}) - f(E_p)}{\omega - (E_{p+q} - E_p) + \mathrm{i}\Gamma} + \xi_- \frac{1 - f(E_{p+q}) - f(E_p)}{\omega + (E_{p+q} + E_p) + \mathrm{i}\Gamma} + \xi_+ \frac{f(E_{p+q}) + f(E_p) - 1}{\omega - (E_{p+q} - E_p) + \mathrm{i}\Gamma}\right) \tag{9}$$

where the coherence factors are given by

$$\xi_0 = \frac{1}{2}\left(1 + \frac{\epsilon_{p+q}\epsilon_p + \Delta_{p+q}\Delta_p}{E_{p+q}E_p}\right)$$
$$\xi_- = \frac{1}{4}\left(1 - \frac{\epsilon_{p+q}}{E_{p+q}} + \frac{\epsilon_p}{E_p} - \frac{\epsilon_{p+q}\epsilon_p + \Delta_{p+q}\Delta_p}{E_{p+q}E_p}\right) \tag{10}$$
$$\xi_+ = \frac{1}{4}\left(1 + \frac{\epsilon_{p+q}}{E_{p+q}} - \frac{\epsilon_p}{E_p} - \frac{\epsilon_{p+q}\epsilon_p + \Delta_{p+q}\Delta_p}{E_{p+q}E_p}\right)$$

When we substitute $\Delta = 0$ in the above, we find that $\xi_0 = 1$, $\xi_- = 0$ and $\xi_+ = 0$ so that, for a vanishing gap (9) reduces to the value of the free paramagnetic electron gas. Here the energy of a particle is given by

$$E_k = [\epsilon_k + \Delta_k^2)^{1/2}. \tag{11}$$

Since the IS [2] is spherically symmetric, we assume that the gap has s-wave symmetry, $\Delta_k = \Delta(T)$.

The uniform susceptibility is given by

$$\chi(0,0) = \frac{\chi_0^{\mathrm{BCS}}(0,0)}{1 - \bar{U}\chi_0^{\mathrm{BCS}}(0,0)} \tag{12}$$

$$\chi_0^{\mathrm{BCS}}(0,0) = N^{-1}\sum_p f(E_p) \tag{13}$$

where $f(E_p)$ is the Fermi distribution function. We define $\Delta(T_c) = 0$ so that $2\Delta(0)/k_B T_c$ becomes a parameter which can be numerically adjusted to fit the experimental data. The Fermi distribution is

$$f(E_p) = [\exp(E_p/k_B T) + 1]^{-1} \simeq \exp(-E_p/k_B T) \simeq 1 - E_p/k_B T$$

but it is not necessary to expand the exponential. The single-particle energy is given by the tight-binding model for the band structure $\epsilon_p = -2t(\cos p_x + \cos p_y) - \mu$ corresponding to atoms in a plane [5] where μ is the chemical potential. We fix the value of t such that $\bar{U} = 2t$. We reduce the calculation of the temperature dependence of the shift to the dimensionless ratio

$$\frac{\delta E_\chi(T)}{\delta E_\chi(T_c)} = \frac{\chi(0,0,T)}{\chi(0,0,T_c)}. \tag{14}$$

We compare our expression of the shift of the Mössbauer line in terms of the susceptibility with the experimentally measured shift of the Mössbauer spectrum of 14.4 keV transition of ^{57}Fe in the superconductors. The experimental measurements of the shift of the Mössbauer spectrum of ^{57}Fe in $Bi_4Sr_3Ca_3Cu_{3.92}Fe_{0.08}O_y$ have been given by Lin and Lin [6]. At low temperatures, $T < 50$ K, there is a reduction in the shift as expected from the temperature dependence of the susceptibility. However, part of the shift which can be assigned to the effect of the susceptibility in this material is quite small. Wu *et al* [2] have performed more detailed measurements of the Mössbauer line shift of ^{57}Fe in the superconducting $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$. We have plotted the centre shift from these data in figure 2. The value at T_c is called $\delta E_\chi(T_c) = 0.24 \pm 0.01$ mm s^{-1} and at $T = 0$ is $\delta E_\chi(0) = 0.20 \pm 0.01$ mm s^{-1}. Therefore, the change in the shift in going from T_c to zero is about $0.04/0.24 \simeq 16.6\%$ which is of the same order of magnitude as expected in going from the normal to the superconducting state. For $\delta E_\chi(T_c) = 0.24$ mm s^{-1} and $2\Delta/k_B T_c = 3.6$ we show the value calculated from (14) together with the measured data. The computed curve is in reasonable agreement with the measured data points considering that error bars are of approximate magnitude ± 0.01 mm s^{-1}. The experimental data thus correspond to $2\Delta/k_B T_c = 3.6$ with $T_c = 62$ K. This value is in reasonable agreement with the value of 3.52 predicted from the BCS theory. The high-temperature $T > T_c$ data show approximately linear behaviour represented by $\delta E(T > T_c) = -2.198 \times 10^{-3} T$ mm s^{-1} which in view of large scatter in the data appears to be in reasonable agreement with the theory of Mössbauer line shifts in normal solids. We have calculated the shift for the s-wave symmetry of the gap: $\Delta_k = \Delta(T)$ consistent with the spherical symmetry of the nuclear potential. Thus our calculation of the IS supports s-wave symmetry for the superconductivity in $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$. Any non-s-electron contributions to the IS can be neglected.

The curvature of the IS as a function of temperature, $-\mathrm{d(IS)}/\mathrm{d}T$, is positive in our theory which uses negative (diamagnetic) susceptibility. However, Wu *et al* [2] drew a curve as a guide to the eye with a curvature of the opposite sign. Therefore, we made an effort to

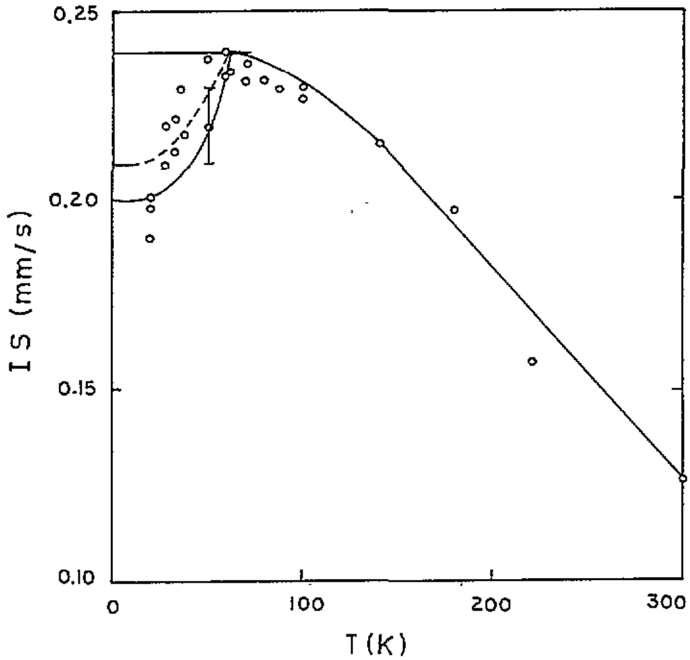

Figure 2. Theoretically calculated Mössbauer line shift as a function of temperature for $T < T_c$ using (14) with $2\Delta/k_BT_c = 3.6$ which shows that the temperature dependence of the shift agrees with that of the susceptibility of a superconductor, leading to a measurement of $2\Delta/k_BT_c$. At high temperatures, $T > T_c$, the behaviour is as expected for normal solids. The experimental points are taken from the work of Wu *et al* [2] who measured the Mössbauer spectra of ^{57}Fe in $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$. Owing to the large scatter in the data the error bars are about 0.01 mm s^{-1}, as indicated on one of the points. The broken curve represent IS= $\delta_{SOD} - a\delta_\chi$.

introduce one more parameter in our theory. We compared the experimental data with two terms, namely a term δ_{SOD} due to the second-order Doppler effect and the other term $a\delta_\chi$ due to the susceptibility; IS $= \delta_{SOD} - a\delta_\chi$ with $a = 0.75$ which is also shown in figure 2. It may be noted that the error bars are of the order of ± 0.01 mm s^{-1} in the measurements of the shifts [7]. It is clear that there is no simple way of changing the curvature of the IS and it should be the same as that of the susceptibility. We expect a small correction due to the possible structural transition below $T_s \simeq 30$ K but this is not reflected by $\chi(T)$ shown in figure 1. If there are any corrections due to the transition at T_s, they will be of no significance to the theory of the IS which remains correct in as far as the proportionality with the susceptibility is concerned. The disagreement between the theory and the experiment may be caused by the fact that in a real material the experimental value may not reach the theoretical value of $-1/4\pi$ as the temperature approaches zero.

The nuclear hyperfine levels relax by absorbing a phonon and emitting another phonon so that the difference between the energies of the emitted and the absorbed phonons is equal to the hyperfine energy A. In this case the relaxation rate is proportional to the product $n_1(n_2 + 1)$ where n_1 and n_2 are the phonon occupation numbers. Since these numbers are large at finite temperatures, $n_1(n_2 + 1) \simeq n_1^2$. Here $n_1 \simeq [\exp(2\Delta/k_BT) - 1]^{-1}$ and $n_2 \simeq \{\exp[(2\Delta + A)/k_BT] - 1\}^{-1}$. The relaxation rate at high temperatures is then given by

$$\frac{1}{\tau} \propto \exp\left(-\frac{4\Delta}{k_B T}\right). \tag{15}$$

Wu *et al* have compared the measured linewidth of the Mössbauer transitions of Fe in $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$ with that expected for a thermally activated process linear in n_l so that

$$\frac{1}{\tau} \propto \exp\left(-\frac{2\Delta}{k_B T}\right) \tag{16}$$

which agrees with the data for $2\Delta/k_B T \simeq 3.6$ in accord with the BCS theory. Wu *et al* found that the mechanism changes at $T_s \simeq 30$ K below which the band gap parameter reduces to 0.6, which is not in agreement with the theoretical value of 3.52. The relaxation between hyperfine levels cannot occur owing to the direct process linear in n_1 because the hyperfine energy, the single-phonon energy and 2Δ are never equal to each other, but the difference between the energies of the two phonons can be equal to the hyperfine energy. Therefore, (15) is much more probable than (16), the use of which affects the measured ratio of $2\Delta/k_B T$. Thus the measured value may be taken to be $2\Delta/k_B T \simeq 1.8$ rather than 3.6 above T_s and 0.3 below it. In the case of a coherent state, the linewidth is to be multiplied by the coherence length ξ and divided by the mean free path l so that [8]

$$\frac{1}{\tau_s} = \frac{1}{\tau_N}\frac{\xi}{l} \simeq \frac{\xi_0}{\tau_N l}\left(1 - \frac{T}{T_c}\right)^{-\nu} \tag{17}$$

where the exponent of the coherence length is $\nu \simeq 0.69$. The normal-state width is $1/\tau_N$ and the superconducting-state linewidth is $1/\tau_s$. At this time, careful measurements of the widths are needed to verify equation (17).

The wavefunction $|\psi(0)|^2$ is a single-atom property [9], which was used earlier to determine the shift of the Mössbauer line. In the case of a solid the phonon effects become important [10]. The line shift depends on the susceptibility in which case the wavevector dependence plays an important role, particularly near the transition temperature. In the case of a superconductor, coherence plays an important role. Therefore, the susceptibility has been introduced in place of the charge density determined by the single-electron wavefunction. In the case of the Mössbauer effect, the recoil is absorbed by the entire lattice. Therefore, the susceptibility of the entire lattice is more relevant than the single-atom charge density. We have reported that the width is related to the coherence length [8, 11]. Later the same idea was published by Mehran and Anderson [12] and by Chakravarty and Orbach [13]. The dependence of the Knight shift on the susceptibility has been discussed in detail by Millis *et al* [14].

In conclusion, we find that the Mössbauer line shift in the superconducting state of $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$ is proportional to the susceptibility calculated from the BCS theory. The temperature dependence of the relative IS agrees with that of the susceptibility. The line shift is consistent with s-wave symmetry of the BCS gap. The high-temperature part of the shift is consistent with that known for normal solids. Thus the Mössbauer line shift is useful for determining the $2\Delta/k_B T_c$ ratio in superconductors.

References

[1] Shrivastava K N 1970 *J. Phys. C: Solid State Phys.* 3 538

[2] Wu Y, Pradhan S and Boolchand P 1991 *Phys. Rev.* **67** 3184
[3] Bardeen J, Cooper L and Schrieffer J R 1957 *Phys. Rev.* **108** 1175
[4] Bulut N and Scalapino D J 1992 *Phys. Rev. Lett.* **68** 706
[5] Kittel C 1976 *Introduction to Solid State Physics* 5th edn (New York: Wiley) p 263
[6] Lin C M and Lin S T 1993 *J. Phys.: Condens. Matter* **5** L247
[7] Boolchand P 1994 private communication
[8] Shrivastava K N 1988 *J. Physique* **49** C8 2239
[9] Shrivastava K N 1976 *Phys. Rev.* B **13** 2782
[10] Shrivastava K N 1973 *Phys. Rev.* B **7** 921; 1970 *Phys. Rev.* B **1** 955
[11] Shrivastava K N 1988 *Solid State Commun.* **68** 1019
[12] Mehran F and Anderson P W 1989 *Solid State Commun.* **71** 29
[13] Chakravarty S and Orbach R 1990 *Phys. Rev. Lett.* **64** 224
[14] Millis A J, Monien H and Pines D 1990 *Phys. Rev. Lett.* B **42** 167