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Abstract
The effect of Cooper pairs on Zn impurity centres at copper sites of the high-temperature superconductor Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ has been revealed by ^{67}Cu(^{67}Zn) emission Mössbauer spectroscopy.

1. Introduction

Superconductivity is reputed to arise due to Cooper pairs. The spatial scale of the pairs (the correlation length) may vary between 10^{-7} and 10^{-4} cm. The appearance of the pairs in the superconducting state and their disappearance in the case of normal conduction may result in changes of electron density at atomic nuclei. This, in turn, leads to Mössbauer isomer shift variation in relation to temperature near T_c. Attempts to detect Cooper pairs in the conventional ('low-temperature') superconductor Nb$_3$Sn by measuring the temperature dependence of the ^{119}Sn Mössbauer isomer shift have failed [1]. This can be explained by a small Δ/Γ value (here Δ is the largest possible difference in isomer shift between two probe states, Γ is the experimental spectral linewidth). For ^{119}Sn Mössbauer spectroscopy (MS), this ratio is <6 [1]. The conditions for detecting Cooper pairs by MS seem to be more favourable for high-temperature superconductors (HTSCs) because of their small correlation lengths. A large Δ/Γ value is desirable for a Mössbauer probe in such experiments. In addition, in choosing objects for study one should take into account the necessity for the probe to be introduced at certain lattice sites. These requirements are satisfied for the ^{67}Zn Mössbauer probe at copper sites of HTSCs when using ^{67}Cu(^{67}Zn) emission MS [2]: firstly, $\Delta/\Gamma \sim 200$ for ^{67}Zn and, secondly, the ^{67}Zn probe occupies copper lattice sites because of its parent ^{67}Cu isotope being certainly placed there during synthesis.

In the present work, ^{67}Cu(^{67}Zn) emission MS investigations were carried out to detect Cooper pairs in the Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ HTSC. For comparison, similar measurements were made with copper oxide; Cu$_2$O exhibits no superconducting transition.

2. Experimental procedure

The samples were synthesized using conventional ceramics technology [3]. The ^{67}Cu radio-active isotope was introduced into Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ by diffusion at 900 °C for one hour, and

into Cu_2O during synthesis. The samples were single phase and $T_c = 22$ K was obtained for $Nd_{1.85}Ce_{0.15}CuO_4$.

The $^{67}Cu(^{67}Zn)$ Mössbauer spectra were recorded in standard transmission geometry using a modified MS-2201 commercial spectrometer. Its electrodynamic drive system was replaced by a piezoelectric drive based on a PZT ceramic. A piezoceramic cylinder was set up in a cylindrical Perspex unit and drove an aluminium container with a ^{67}ZnS absorber (surface density 1 g cm^{-2} in terms of ^{67}Zn). The sources were fixed at the other end of the Perspex unit. The integrated and amplified low-frequency drive signal of the basic spectrometer was used to produce motion. No feedback was employed in the drive system. A velocity range of up to 150 μs^{-1} was scanned. The velocity scale was calibrated against the quadrupole hyperfine pattern of ^{67}ZnO.

The absorber and the sources were placed in separate volumes of the Perspex unit. Both the absorber and the source were cooled by a helium gas flow. Their temperatures were measured by semiconductor devices. The absorber and the piezoceramic cylinder were kept at 10(2) K, whereas the source temperature could be raised to 60 K and controlled with the same accuracy. The gamma radiation of the ^{67}Cu was recorded with a Ge(Li) detector sensitized to the 100 keV region.

More experimental details will be given in [4].

3. Experimental results

Figures 1 and 2 show typical spectra and results of their processing, respectively. The Mössbauer spectra of both $Nd_{1.85}Ce_{0.15}CuO_4$ and Cu_2O are well-resolved quadrupole triplets throughout the whole temperature range. Their isomer shifts correspond to Zn^{2+}. It seems obvious that the daughter ^{67}Zn atoms remain at copper sites after the decay of the ^{67}Cu parent isotope. Since copper atoms occupy a single kind of site in the $Nd_{1.85}Ce_{0.15}CuO_4$ lattices [5], it was expected that the $^{67}Cu(^{67}Zn)$ Mössbauer spectra for both the compounds would correspond to single states of the Zn^{2+} Mössbauer probe. This is actually the case for the experimental spectra. Both of the spectra in figure 1 are characterized by an asymmetry parameter $\eta \sim 0.2$, with quadrupole coupling constants $C = eQU_{zz}$ of +15.3(3) MHz and −22.0(5) MHz for
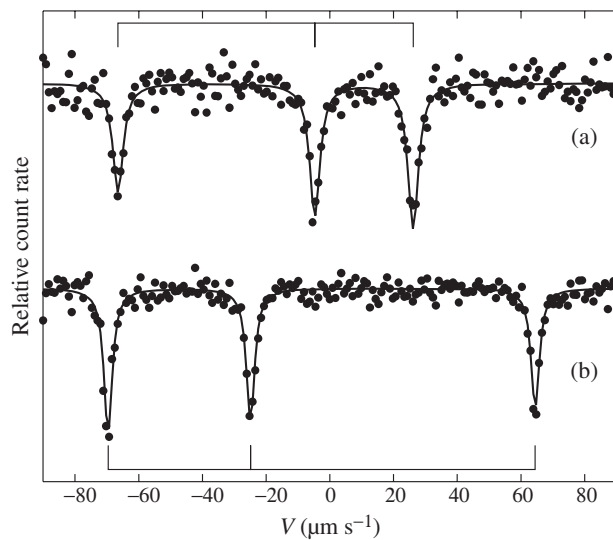

Figure 1. $^{67}Cu(^{67}Zn)$ Mössbauer emission spectra of (a) $Nd_{1.85}Ce_{0.15}CuO_4$ and (b) Cu_2O at 10 K. The components of the quadrupole triplets corresponding to $^{67}Zn^{2+}$ centres at copper sites are shown.
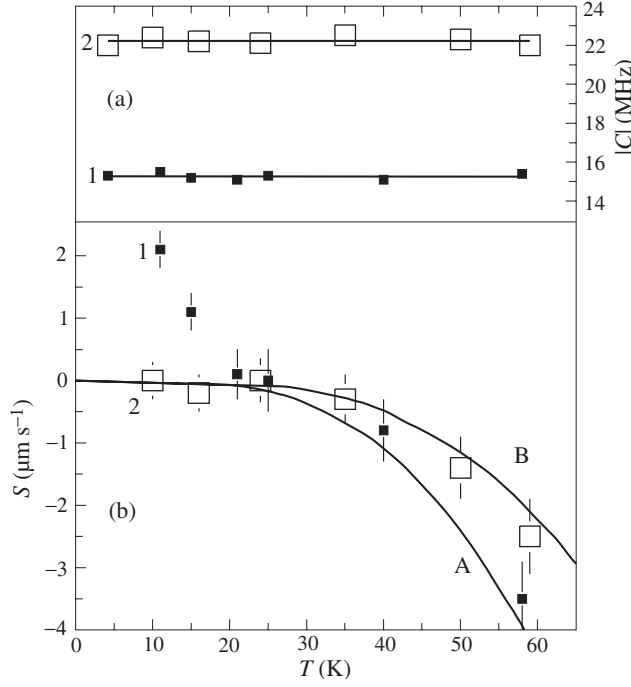
Figure 2. (a) Temperature dependences of the ^{67}Zn quadrupole interaction constant C for Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ (curve 1) and Cu$_2$O (curve 2). The data for 4.2 K are taken from [3]. (b) The temperature dependences of the ^{67}Zn Mössbauer spectrum centroid position S measured relative to its value at 22 K for Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ (curve 1) and Cu$_2$O (curve 2). Curves A and B show the temperature dependences of the second-order Doppler shift calculated for $\theta = 300$ K (curve A) and $\theta = 400$ K (curve B).

Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ and Cu$_2$O, respectively. Here Q is the quadrupole moment of the ^{67}Zn nucleus and U_{zz} is the principal component of the electric field gradient (EFG) tensor at this nucleus.

Figure 2(a) shows the temperature dependence of the quadrupole interaction constant. It is seen that C is practically temperature independent for both Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ and Cu$_2$O. The 4.2 K data of [3] are also plotted in figure 2(a). The independence of eQU_{zz} of temperature seems to be expectable, because the EFG at the ^{67}Zn^{2+} probe is produced by lattice ions only and the variations of cell unit parameters are negligibly small in the range from 4.2 to 60 K [5].

The temperature dependences of the spectrum centroid positions S are shown in figure 2(b) as measured relative their values at 22 K. They are essentially different for Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ and Cu$_2$O although no abrupt changes in S are observed for Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ near T_c.

4. Discussion

The temperature dependence of S is determined at constant pressure by the following three terms [6]:

$$\left(\frac{\delta S}{\delta T}\right)_P = \left(\frac{\delta I}{\delta \ln V}\right)_T \left(\frac{\delta \ln V}{\delta T}\right)_P + \left(\frac{\delta D}{\delta T}\right)_P + \left(\frac{\delta I}{\delta T}\right)_V. \tag{1}$$

The first term in equation (1) represents the dependence of the isomer shift on the volume increase during thermal expansion of the lattice. Calculations have shown [7] that this term is

negligible for ^{67}Zn within the above temperature interval ($<0.03\ \mu$m s^{-1}) and structural phase transitions are revealed neither for $Nd_{1.85}Ce_{0.15}CuO_4$ nor for Cu_2O [5].

The second term in equation (1) describes the second-order Doppler shift D. It can be written in the Debye approximation [8] as

$$\left(\frac{\delta D}{\delta T}\right)_P = -\frac{3kE_0}{2Mc^2}F\left(\frac{T}{\theta}\right) \tag{2}$$

where E_0 is the excited-state energy, k is the Boltzmann constant, M is the mass of the probe nucleus, c is the speed of light in vacuum, θ is the Debye temperature and $F(T/\theta)$ is the Debye function.

As is seen from figure 2(b), the experimental data for Cu_2O in the 10 to 60 K range and for $Nd_{1.85}Ce_{0.15}CuO_4$ at $T > T_c$ are satisfactorily described by equation (2) with θ-values between 300 to 400 K, whereas θ is known to be $\sim$300 K for $Nd_{1.85}Ce_{0.15}CuO_4$ [9].

Finally, the third term in equation (1) describes the temperature dependence of the isomer shift I at constant volume. It is caused by variations of the s-electron density at the ^{67}Zn nuclei, which are not associated with thermal expansion of the lattice. This effect is expected to occur at a transition of the matrix to the superconducting state. The increase in S with decreasing temperature at $T < T_c$ indicates an increase in the electron density at the ^{67}Zn nuclei.

In other words, the temperature dependence of S for the $Nd_{1.85}Ce_{0.15}CuO_4$ superconductor is determined at $T > T_c$ by the second-order Doppler shift, and at $T < T_c$ by the increase in the ^{67}Zn probe electron density, induced by the superconducting transition.

The Zn probe is a two-electron centre with negative correlation energy, so its charge state can be altered only by a simultaneous transition of two electrons. Unfortunately, no clear models are currently available to describe the change in the electron density at nuclei for impurity probes in superconductors below T_c. For our case, it might be regarded as a change in the charge state (oxidation level) of the Zn probe. However, this interpretation encounters two difficulties. Firstly, the observed magnitude of S ($\approx$2 μm s^{-1}) is much smaller than the isomer shift value of $\approx$160 μm s^{-1} expected for the $Zn^{2+} \rightarrow Zn^0$ recharging [10]. This difficulty may be overcome by supposing some effective length larger than the Zn atomic radius—for instance, that of a Cooper pair—as the electron pair localization radius. Secondly, the impurity charge is determined by the Fermi level position relative to the one-electron energy level associated with the Zn impurity. At $T > T_c$, the Fermi level must lie considerably lower than the Zn level. By contrast, the observed temperature dependence of S at $T < T_c$ means that the Fermi level lies within about kT, i.e. $\approx$1 meV at these temperatures, of the Zn level. Another interpretation supposes that the observed increase in the electron density reveals a change in the spatial distribution of electrons in Cooper pair creation and the temperature dependence of the Bose condensate fraction. The problem arising from such an approach concerns the ability of an impurity probe to detect these changes. An electron pair localized at the ^{67}Zn centre has zero values of the total, orbital and spin angular momenta. On the other hand, the BCS theory requires pairing of electrons with opposite kinetic momenta, so the total kinetic, total angular and spin momenta are zero for the pair. The combination of these factors seems to create conditions for Cooper pair electron density spreading over the ^{67}Zn probe.

5. Conclusions

For the $Nd_{1.85}Ce_{0.15}CuO_4$ superconductor, the temperature dependence of the ^{67}Zn Mössbauer spectrum centroid S is determined in the temperature range $T > T_c$ by the second-order Doppler shift, and at $T < T_c$ by the effect of the Bose condensation on the ^{67}Zn probe electron density. The S-value increases with decreasing temperature.

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