Superconducting properties of AgSnSe₂ studied by ⁷⁷Se-NMR and ¹¹⁹Sn-NMR

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We studied the superconducting properties of AgSnSe₂ by ⁷⁷Se-NMR and ¹¹⁹Sn-NMR. This compound has strong disorder, because Ag and Sn atoms randomly occupy the cation sites. The Knight shifts of the ⁷⁷Se-NMR and ¹¹⁹Sn-NMR spectra decrease in the superconducting state, which indicates that AgSnSe₂ is a spin-singlet superconductor. The result of ¹¹⁹Sn-NMR also shows that the ¹¹⁹Sn-Knight shift does not completely vanish even in the low temperature limit. This suggests that spin and orbital are strongly entangled in this superconducting state owing to the synergetic effect of the strong spin-orbit interaction and strong scattering by the disorder inherent in this compound.

KEYWORDS: unconventional superconductivity, strong disorder, spin-orbit interaction,

1. Introduction

In the conventional s-wave superconductivity, random potential due to impurities or lattice disorder does not change a majority of superconducting properties such as transition temperature and energy gap, unless it breaks time-reversal symmetry. This is called Anderson's theorem [1].

A type-II superconductor AgSnSe₂ has attracted attention recently. This material has a Ginzburg-Landau parameter as large as 55, and has a NaCl-type crystal structure [2]. One issue discussed in this material is the possibility of the valence skipping [3] because the nominal valence of Sn in this compound is +3, which is usually forbidden. The other issue in this material is a strong disorder effect. The mean free path is reported to be as short as 9 Å even in low-temperature limit [2], which is comparable to the lattice constant of the system (5.675 Å), suggesting a presence of strong scattering. This is because Ag and Sn atoms randomly occupy the cation position in the crystal structure [2]. The relationship between this strong disorder and the superconducting nature in this material has not been clarified and is attracting interest.

In this paper, we report superconducting properties microscopically clarified by ⁷⁷Se-NMR and ¹¹⁹Sn-NMR measurements performed under low magnetic fields that do not destroy the superconductivity.
2. Experiment

Polycrystalline Ag\textsubscript{1-x}Sn\textsubscript{1+x}Se\textsubscript{2} crystals were synthesized by a conventional melt growth method. The compound studied here is Ag\textsubscript{0.8}Sn\textsubscript{1.2}Se\textsubscript{2}, where the highest superconducting transition temperature ($T_c = 6.9$ K) has been observed [5]. They were ground into grains of 100 to 700 micrometers in size to prevent the reduction of the NMR signal by the radio-frequency skin effect. Before the main NMR measurements, we performed ac susceptibility measurements to check $T_c$ of the samples used for the NMR measurements. To estimate the ac susceptibility, we measured the resonance frequency of the LC tank circuit shown in Fig. 1. We performed the ac susceptibility measurements in the two conditions: i) without applied dc magnetic field, and ii) with a dc magnetic field of 1.39 T applied perpendicular to the ac magnetic field (this is almost the same condition for the $^{77}$Se- and $^{119}$Sn-NMR measurements).

The spectra of $^{77}$Se- and $^{119}$Sn-NMR were obtained by a Fourier transformation of the spin-echo signals following a $\pi/2$-$\pi$ pulse sequence under 1.35 T and 1.39 T, respectively, which are sufficiently weak to survive the superconductivity. To avoid heating effect, the samples were immersed directly in liquid He in the low temperature measurements. The widths of the $\pi/2$ - $\pi$ pulses for the $^{77}$Se-NMR and $^{119}$Sn-NMR measurements were typically 8.5 - 17 $\mu$s and 1.5- 3 $\mu$s, respectively. As for the $^{119}$Sn-NMR spectra, although the frequency range to be covered by these pulses is within approximately ±100 kHz, the observed NMR spectra are broadened beyond this range; therefore, we measured spin-echo signals at various frequencies with an interval of 80 kHz, and the entire spectra were then constructed by combining these local spectra.

We measured the spin-lattice relaxation rate $T_{1^{-1}}$ of the $^{77}$Se nuclei by the standard saturation recovery method. We determined $^{77}$Se $T_{1^{-1}}$ by fitting the spin-echo intensity $M(t)$ after a time delay $t$ following saturation comb pulses to single-exponential function $\frac{1-M(t)}{M(\infty)} = \exp(-t/T_1)$. 

![Fig. 1. LC tank circuit for the ac susceptibility measurement. The same circuit was also used for the $^{77}$Se-NMR and $^{119}$Sn-NMR measurements.](image-url)
3. Results and Discussion

3.1 ac susceptibility

Figure 2 shows the temperature dependence of the ac susceptibility of our samples. The data without dc magnetic field shows that the onset of $T_c$ is around 6.0 K. Note that the diamagnetic signal grows rather gradually. One reason for this gradual growth is the magnetic penetration effect. Around $T_c$, the penetration length $\lambda$ tends to diverge and becomes comparable to the powder sample size, which suppresses the diamagnetic signal. However, we think that this effect alone cannot explain completely the present gradual growth of the diamagnetism. The other important reason is the distribution of $T_c$. Because the diamagnetism grows down to 4 K, it is natural to think that $T_c$ is distributed from 6 K to 4 K.

When we apply a dc magnetic field of 1.39 T (which is almost the same magnetic field for the $^{77}\text{Se-NMR}$ and $^{119}\text{Sn-NMR}$ measurements discussed below), the onset of $T_c$ decreases to 4.4 K. Note that the ac diamagnetism under the dc magnetic field is not due to the simple Meissner effect but due to the pinning of the vortices tilting motion and thus it is impossible to estimate the superconducting volume fraction from the data.

![Fig. 2. Temperature dependence of the ac susceptibility of AgSnSe$_2$. The unit of the vertical axis is arbitrary.](image)

3.2 $^{77}\text{Se-NMR}$

Figure 3(a) shows the temperature dependence of the $^{77}\text{Se-NMR}$ spectrum under a low magnetic field of 1.35 T, which does not destroy the superconductivity. The origin of the horizontal axis represents the unshifted resonance frequency of $^{77}\text{Se}$ bare nuclei. While a positive shift of $\sim$1000 ppm is observed in the normal state, it decreases on cooling in the superconducting state, as clearly shown in Fig. 3 (b). This is the first microscopic evidence that the superconductivity in this compound is spin-singlet.

Note that, however, it is impossible to precisely estimate the Knight shift or spin susceptibility from the $^{77}\text{Se-NMR}$ data, because the present shift is caused not only by the Knight shift but also by the chemical shift. The order of the chemical shift of $^{77}\text{Se-NMR}$ spectra is typically $10^2$-$10^3$ ppm, which is the same order of the presently observed shift. In the present case, we do not know the precise value of the chemical shift and thus do not know the precise position of the Knight shift origin. Therefore we cannot estimate quantitatively how much the Knight shift decreases in the superconducting state, although
its decrease leaves no room for doubt and thus we can conclude that this is a spin-singlet superconductivity.

Figure 4 shows the temperature dependence of the $^{77}$Se nuclear spin-lattice relaxation rate divided by the temperature, $1/T_1T$. In addition to the data obtained at 1.35 T, for comparison, we show the data obtained at 8.70 T, which is so strong that the superconductivity is completely destroyed down to the lowest measured temperature. The data for 8.70 T shows an almost constant value of $1/T_1T$, following the Korringa relation. In contrast, the data for 1.35 T shows a rapid decrease as the temperature is decreased below 4.4 K. This decrease clearly indicates the formation of the superconducting gap. At the lowest measured temperature 1.4 K, the value of $1/T_1T$ is decreased to $1/3 - 1/4$ of its high-temperature Korringa value. Note that a coherence peak was not observed. This is probably due to the distribution of $T_c$ discussed in the previous section, which causes the coherence peak structure to be smeared.

![Fig. 3. (a) Temperature dependence of the $^{77}$Se-NMR spectrum under a low magnetic field of 1.35 T. (b) Temperature dependence of the 1st moment of the $^{77}$Se-NMR spectrum shown in Fig. 3(a).](image)

![Fig. 4. Temperature dependence of the $^{77}$Se nuclear spin-lattice relaxation rate divided by the temperature, $1/T_1T$.](image)
3.3 $^{119}$Sn-NMR

To obtain more reliable spin susceptibility information, we measured $^{119}$Sn-NMR spectrum. Figure 5(a) shows the temperature dependence of the $^{119}$Sn-NMR spectrum under a low magnetic field of 1.39 T, which is almost the same field as the $^{77}$Se-NMR measurement described in the previous section. The shift observed in the normal state is approximately 25000 ppm, which is 25 times bigger than that for the $^{77}$Se-NMR data. This indicates that the conducting electrons are mainly on the Sn-5s orbital, which causes strong hyperfine field on the $^{119}$Sn nuclei. Because of this strong hyperfine coupling, the shift of the $^{119}$Sn spectra is almost completely dominated by the Knight shift and is hardly affected by the chemical shift. Thus, we can estimate precisely the temperature dependence of the spin susceptibility from the $^{119}$Sn data. Figure 5(b) shows the temperature dependence of the $^{119}$Sn-NMR shift, which can be regarded as the spin susceptibility. We can see that the shift decrease as the temperature is decreased, which is also the case with the $^{77}$Se-NMR data.

The important point to note here is that the shift does not completely vanish even in the low temperature limit. The shift at 1.6 K is about 18000 ppm, which is as large as 70% of that in the normal state. This suggests that a considerable amount of the spin susceptibility survives even deep in the superconducting state. This is not attributable to a residual density of state, because $^{77}$Se-NMR $1/T_1 T$, which measures the square of the density of states, shows a much stronger decrease as explained in the previous section. Therefore, the residual spin susceptibility in the deep superconducting state is caused not by a residual density of state but by a Van-Vleck type mixing effect. Indeed, it has been proposed that the presence of both strong spin-orbit interaction and disorder generally restores spin susceptibility in superconducting states by the mixing effect [6,7]. In this scenario, the disorder induces spin-flip scattering through the spin-orbit interaction. Consequently, the orbital wave function and spin wave function of Bloch electrons are strongly entangled, and spin operator $S_z$ is no longer a good quantum number. In this case, Cooper pairs are composed of these (time-reversal partner) Bloch electrons that are not the eigenstates of $S_z$, and thus cause nonzero spin susceptibility by the mixing effect under an applied magnetic field.

![Fig. 5](https://journals.jps.jp/011057-5)

**Fig. 5.** (a) Temperature dependence of the $^{119}$Sn-NMR spectrum under a low magnetic field of 1.39 T. (b) Temperature dependence of the 1st moment of the $^{119}$Sn-NMR spectrum shown in Fig. 5(a)
4. Conclusion

We performed $^{77}\text{Se}$- and $^{119}\text{Sn}$-NMR measurements in order to clarify the superconducting state of AgSnSe$_2$. We observed that the Knight shifts of the $^{77}\text{Se}$-NMR and $^{119}\text{Sn}$-NMR spectra decrease as the temperature is decreased. Therefore, we concluded that this material is a spin-singlet superconductor. However, the Knight shift of the $^{119}\text{Sn}$-NMR spectrum or the spin susceptibility does not completely vanish even in the low temperature limit. This suggests that spin and orbital wave functions are strongly entangled owing to the synergetic effect of the strong spin-orbit interaction and scattering by the disorder inherent in this material, which restores the spin susceptibility in the superconducting state by a mixing effect.

References