Magnetic fluctuations in $FeSe_{1-\delta}$ and Cu-doped $FeSe_{1-\delta}$: ^{77}Se NMR experiments

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The roles of Se deficiency and Fe atoms, for the superconductivity of FeSe, have been, respectively, investigated in $FeSe_{1-\delta}$ and $(Fe_{1-x}Cu_x)Se_{1-\delta}$, by our NMR experiments. The data, for nuclear spin-lattice relaxation rate $(1/T_1)$, show that the spin fluctuations are weakened at a larger δ, and are correlated with the superconductivity in FeSe. The superconducting volume fraction, estimated by our ac susceptibility experiments, is found to vary inversely with δ. Our findings suggest that the Se-deficient FeSe has an inhomogeneous phase, where the superconductivity is associated with the regions having few or no Se vacancies. As for $(Fe_{1-x}Cu_x)Se_{1-\delta}$, T_c is rapidly suppressed by Cu doping and vanishes around $x=0.03$. The ^{77}Se and the ^{63}Cu NMR linewidths suggest that a local moment is induced at the Fe sites and not at the Cu sites. However, $1/T_1$ shows no obvious change with the Cu doping. We suspect that other effects, such as disorder or change in the density of states, have more influence on T_c suppression since a metal-insulator transition, induced by Cu substitution, occurs in the resistivity measurements.

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Among the discovered iron-based superconductors, $FeSe_{1-\delta}$ was a binary compound to be found.[1] Though its superconducting temperature, $T_c \sim 8$ K, is not as high as those in the class of iron-arsenic superconductors, $FeSe_{1-\delta}$ has quickly drawn considerable attention, due to its structural simplicity and easier material handling. Recent high-pressure experiments have even raised its T_c up to 36.7 K, which is comparable to the FeAs-based superconductors.[2] This has made FeSe a potential paradigm for investigating the mechanism of superconductivity in the Fe-based superconductors. Indeed, FeSe has been found to share a number of features with the FeAs-based superconductors, including layered structures, electronic states, and lattice instability.[3–5] However, still unclear is whether or not FeSe is similar to the iron arsenides, with regard to spin-density-wave instability or magnetic order.[2,6] Recent high-pressure NMR experiments, on the other hand, have demonstrated strong spin correlation with the superconductivity in FeSe, as also found in other iron arsenides.[7,8] Further investigation must determine whether or not the spin-fluctuation-driven picture, of the Cooper-pairing mechanism, is applicable to the Fe-based superconductors. Here, we report our NMR studies on the Se-deficient and Cu-substituted FeSe.

Iron selenide has complex structural phases, as summarized in the original literature where the superconductivity was reported in the Se-deficient tetragonal β-FeSe, i.e., $FeSe_{0.82}$ and $FeSe_{0.88}$.[1] A similar finding soon followed, for a composition of $FeSe_{0.92}$.[9] However, McQueen *et al.* have recently claimed that the superconductivity actually exists only in the nearly stoichiometric FeSe and a small Se deficiency ($\delta=0.03$) is enough to destroy the Cooper pairing.[10] Though they attributed this discrepancy to the oxygen contamination in those Se-deficient samples, it is intriguing to ask why any oxygen contamination, in $FeSe_{0.88}$ and $FeSe_{0.92}$, would produce a similar T_c as $FeSe_{0.99}$. Clarifying the role of Se deficiency, in FeSe, is crucial to any theoretical treatments of the pairing mechanism because it determines whether or not it is essential to introduce charge carriers in the two-dimensional (2D) FeSe layers, as compared to the cuprate superconductors.

The role of the Fe^{2+} spin is another interesting issue, which has recently been investigated by chemically substituting Fe for Cu, i.e., $(Fe_{1-x}Cu_x)Se_{1-\delta}$.[11,12] The superconductivity is rapidly suppressed by the Cu doping and is followed by a metal-insulator transition. Cu^{2+} and Fe^{2+} have the same valence electrons but posses different spins and atomic radii. This chemical substitution is generally expected to alter the lattice and electronic structures, to introduce disorder and modify spin correlation. However, which one most dominates needs clarification.

We have conducted experiments for ^{77}Se NMR spectrum and nuclear spin-lattice relaxation rate $(1/T_1)$, on Se-deficient $FeSe_{0.88}$ and Cu-doped $(Fe_{1-x}Cu_x)Se_{1-\delta}$, to investigate the role of Se deficiency and magnetic correlation in FeSe. Our findings suggest that spin fluctuations are closely related to the superconductivity in FeSe, as previously reported by Imai *et al.*[7] Our $1/T_1$ and superconducting volume fraction analysis indicate that the Se-deficient FeSe has an inhomogeneous electronic state, where the pairing occurs only in the regions having few or no Se vacancy, expanding upon similar results from previously reported NMR data. This is supported by the decrease in spin fluctuation and superconducting volume fraction at larger δ. As for $(Fe_{1-x}Cu_x)Se_{1-\delta}$, we find that the NMR linewidth increases drastically upon Cu doping and then saturates. Whether or not this Cu-induced disorder is correlated with the rapid suppression of T_c needs further investigation. Interestingly, the $1/T_1$ is nearly unchanged upon Cu doping. We suspect that the electronic band structure is altered more significantly than the spin dynamics because a metal-insulator transition was shown in the resistivity measurements.[1]

Polycrystalline samples of the Se-deficient $FeSe_{0.88}$ and the Cu-substituted $(Fe_{1-x}Cu_x)Se_{1-\delta}$ with $(x,\delta)=(0,0.12)$, (0.01, 0.15), (0.02, 0.12), (0.03, 0.12), and (0.04, 0.12) were used in our NMR and ac magnetic-susceptibility experiments. Sample preparation was similar to that of $(Fe_{1-x}Cu_x)Se_{0.85}$ in Ref. 11. Figure 1 gives the powder x-ray diffraction patterns of these samples. Rietveld refinement was analyzed by using GSAS software, to confirm the sample stoichiometry and quality. Detailed structural analysis shows

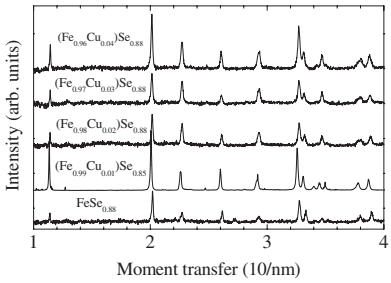

FIG. 1. Powder x-ray diffraction patterns of $(Fe_{1-x}Cu_x)Se_{1-\delta}$. The horizontal axis is the moment transfer, $M=4\pi \sin(\theta)/\lambda$.

similar features as for $(Fe_{1-x}Cu_x)Se_{0.85}$ in Ref. 11. Figure 2 shows the resistivity (normalized to 300 K) of different Cu contents. As in $(Fe_{1-x}Cu_x)Se_{0.85}$ and $(Fe_{1.01-x}Cu_x)Se$, a metal-insulator transition is also observed in our $(Fe_{1-x}Cu_x)Se_{0.88}$ samples.[11,12]

To our knowledge, there are only three NMR papers, to date, reporting on superconductivity in $FeSe_{1-\delta}$. Imai *et al.* measured the nearly stoichiometric $FeSe_{0.99}$ and $FeSe_{0.97}$, with the samples claimed to be free of oxygen contamination.[7] Kotegawa *et al.*[13] and Masaki *et al.*[8] studied the Se-deficient $FeSe_{0.92}$ but did not specify whether or not there was any oxygen contamination. In order to resolve the discrepancy, regarding the stoichiometry of the superconductivity in FeSe, the following discussions compare our $FeSe_{0.88}$ data, with the data reproduced from the previous literature. Standard Hahn-echo pulse sequences and saturation pulses were, respectively, employed throughout our ^{77}Se NMR spectra and $1/T_1$ experiments at 75 kG.

Figure 3 shows the ^{77}Se NMR spectra of $FeSe_{1-\delta}$ at 10 K. The linewidth increases with the Se deficiency, as expected because NMR linewidth generally reflects the amount of lattice disorder in the sample. This indirectly confirms the correct stoichiometry of these samples. Similar $T_c \approx 8$ K, observed in the disordered $FeSe_{0.88}$ and ordered $FeSe_{0.99}$, suggests that the Cooper pairing is not vulnerable to the lattice disorder induced by the Se vacancy. We notice that the frequency shift (K) does not vary much with δ (Fig. 3, inset), which means that the local spin susceptibility χ does not change much either because $K \propto \chi$. These results differ from those, in the report on bulk susceptibilities, by Williams *et al.*, in which bulk susceptibility increases significantly with δ, due to the impurity phases from excess Fe or iron oxides. If these magnetic impurities were bonded to the FeSe samples, magnetic broadening of the linewidth would also be

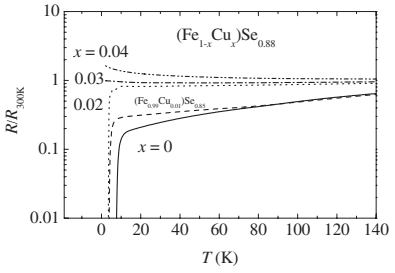

FIG. 2. Resistivity (R) data for different Cu-substituted $(Fe_{1-x}Cu_x)Se_{1-\delta}$ samples. Data have been normalized to room-temperature values $(R_{300\ K})$.

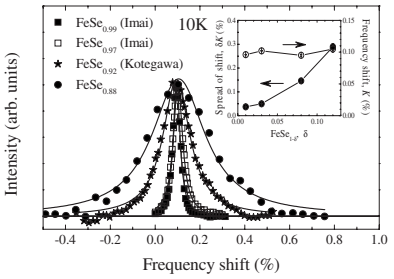

FIG. 3. ^{77}Se NMR spectra, at 10 K, for different Se-deficient $FeSe_{1-\delta}$. Data for $FeSe_{0.97\&0.99}$ and $FeSe_{0.92}$ are reproduced from Refs. 7 and 13, respectively. Inset: frequency shift and the spread of shift, derived from the spectra.

seen at low temperature. The linewidth for our $FeSe_{0.88}$ is nearly temperature independent, from 70 K down to T_c (not shown), as was the case for $FeSe_{0.92}$ in Ref. 13. Therefore, our NMR frequency shift and linewidth data suggest that any impurity phases would not enter the $FeSe_{1-\delta}$ stoichiometry but we cannot rule out the possibility of oxygen contamination in $FeSe_{1-\delta}$, as McQueen *et al.*[10] pointed out, for $FeSe_{1-\delta}O_y$. We will leave this issue to a later discussion.

Figure 4 displays a typical nuclear spin-lattice relaxation curve [$M(t)$: nuclear magnetization as a function of time] for $FeSe_{0.88}$ at 16 K. Stretched exponential behavior $[e^{-(t/T_1)^{\alpha}}]$ is observed, in contrast to the single exponential in $FeSe_{0.99}$ and $FeSe_{0.97}$.[7] This means that T_1 is distributed in $FeSe_{0.88}$, due to Se-vacancy-induced disorder. We note that the single exponential, in the nearly stoichiometric FeSe polycrystal samples, implies a nearly isotropic T_1, although it possesses a 2D layered structure. A stretched exponential, caused by anisotropic T_1, is then ruled out. The inset shows the stretched exponent (α) obtained from a stretched exponential curve fitting. This temperature-dependent exponent implies that different Se sites have different temperature-dependent $1/T_1$. Similar behavior was also reported in $FeSe_{0.92}$.[13]

The relaxation rate from the stretched fit is plotted in Fig. 5. The Korringa-type behavior $(T_1T=\text{const})$, for temperatures between T_c and 50 K, in $FeSe_{0.88}$ and $FeSe_{0.92}$, is actually misleading because both $1/T_1$ values are directly from the stretched exponential fit. These stretched data cannot reflect the true average behavior for $1/(T_1T)$ since the stretched exponent is known to be temperature dependent. Masaki *et al.* have fit their $FeSe_{0.92}$ relaxation curves, using a

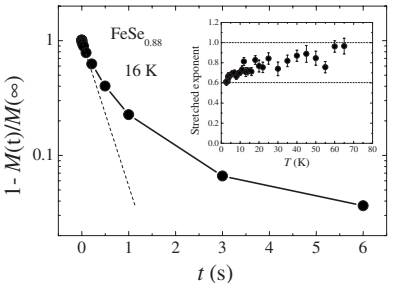

FIG. 4. ^{77}Se nuclear spin-lattice relaxation curve for $FeSe_{0.88}$ at 16 K [$M(t)$: nuclear magnetization]. Dashed line: single exponential curve. Inset: stretched exponent from the stretched exponential curve fitting $[e^{-(t/T_1)^{\alpha}}]$.

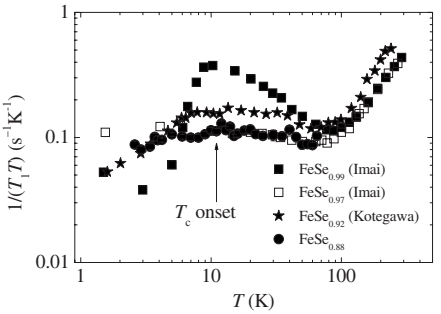

FIG. 5. Plot of ^{77}Se $1/(T_1T)$ as a function of temperature. Data for $FeSe_{0.97}$ and $FeSe_{0.99}$ are single-T_1 values reproduced from Ref. 7. Data for $FeSe_{0.92}$ (reproduced from Ref. 13) and $FeSe_{0.88}$ are stretched-T_1 values (see text).

two-T_1 function, and found that the short T_1 component displays an enhanced $1/T_1$ that is similar to $FeSe_{0.99}$.[8] The upward $1/(T_1T)$, just above T_c, has been considered as evidence for the connection of spin fluctuations to superconductivity in FeSe.[7] In order to catch the intrinsic feature from the distributed T_1, we calculated the average $1/T_1$, directly from the initial slope of the relaxation curve,[14] instead of the two-T_1 fit. Figure 6 (filled circles) gives the average $1/(T_1T)$ data for our $FeSe_{0.88}$. Indeed, similar uprising behavior, at low temperature, is seen in our sample, in contrast to the flat behavior in the nonsuperconducting $FeSe_{0.97}$. Note that the drop of $1/(T_1T)$ below T_c, expected from the opening of the superconducting gap, is smeared out due to the broad $1/T_1$ distribution.

We can see that the size of the spin fluctuations seems to decrease with δ, for the superconducting samples, by looking at the $1/(T_1T)$ value just above T_c (Fig. 5). If the magnetic fluctuations are strongly linked to the Cooper pairing in FeSe, why do $FeSe_{0.99}$, $FeSe_{0.92}$, and $FeSe_{0.88}$ show similar onset T_c? The superconducting volume fraction estimated from our ac susceptibility experiment may provide a clue. Figure 7 (open circles) shows our dynamical magnetic-susceptibility data for $FeSe_{0.88}$. It was measured by using the LC resonant circuit originally for NMR experiments.[7] This method utilizes the resonance frequency ω ($\sim 1/\sqrt{LC}$) of the LC circuit which changes with the inductance, which in turn depends on the sample susceptibility χ. That is, $L=L_0[1+4\pi\chi(T)]$, L_0: inductance of the NMR coil. The rising of the frequency-shift ratio [defined as $\omega(T)/\omega(15)-1$] in Fig. 7 represents the superconducting transition because ω increases as it enters the superconducting state, $\chi<0$. The size

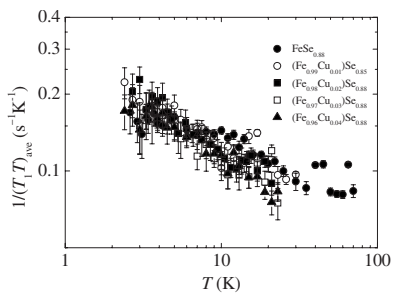

FIG. 6. The average $(T_1T)^{-1}$, of ^{77}Se in $(Fe_{1-x}Cu_x)Se_{1-\delta}$, measured at 60.99 MHz ($\sim$75 kG).

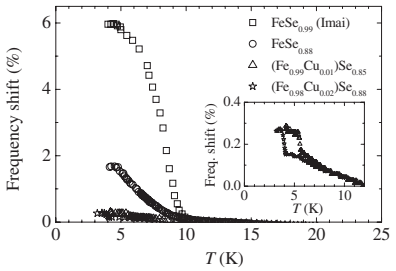

FIG. 7. Data for the ac magnetic susceptibilities of $FeSe_{0.99}$ (reproduced from Ref. 7), $FeSe_{0.88}$, $(Fe_{0.99}Cu_{0.01})Se_{0.85}$, and $(Fe_{0.98}Cu_{0.02})Se_{0.88}$. The frequency shift, on the vertical axis, is explained in the text.

of the frequency-shift ratio gives a rough estimate of the superconducting volume fraction.

We found that $FeSe_{0.88}$ has a superconducting volume fraction significantly smaller than $FeSe_{0.99}$ since $FeSe_{0.88}$ has a smaller frequency-shift ratio. The dc bulk susceptibilities, reported in Ref. 12, show the similar result of a weaker superconducting diamagnetic response in $FeSe_{0.82}$, if the background signal from impurities is subtracted. Note that the pressure experiment on $FeSe_{0.99}$ shows that T_c and superconducting volume fraction vary simultaneously with pressure,[7] unlike in the Se-deficient case, where only superconducting volume fraction varies with Se deficiency. We also did the two-T_1 analysis for our $FeSe_{0.88}$ and found that the volume fraction, for the short T_1 component, is about 50%, which is 10% less than that in $FeSe_{0.92}$.[8]

Combining the reduced superconducting volume fraction in the Se-deficient FeSe with the findings from the previous discussions, i.e., the different temperature-dependent $1/T_1$ at different Se sites and the reduced spin fluctuations at a larger δ, we infer that the Se-deficient FeSe has an inhomogeneous phase, where the superconductivity comes from regions with few or no Se vacancies. The Se-vacancy-free region has much stronger magnetic fluctuations than the Se-vacant region. When greater vacancy is introduced in FeSe, both the overall spin fluctuations and superconducting volume fraction decrease. However, this picture cannot explain why the superconductivity disappears in $FeSe_{0.97}$.[10] Is this really due to the oxygen contamination in those Se-deficient samples so that the superconductivity is actually from $FeSe_{1-\delta}O_y$, instead of $FeSe_{1-\delta}$? An oxygen-free $FeSe_{0.82}$ has been reported by Williams *et al.*, with magnetic susceptibility clearly showing a superconducting diamagnetic response, if the background signal from impurities is subtracted.[12] Therefore, we think it unlikely that occurrence of any oxygen contamination is the cause. While preparing this paper, we noticed that a different result was recently reported, where the superconductivity was claimed to exist in a narrow range of $\delta=0.03$, i.e., $FeSe_{0.974\pm0.005}$.[15] These recent experiments, together with our own, indicate that the superconductivity emerges from the nearly stoichiometric FeSe.

Figure 8(a) shows the ^{77}Se NMR spectra in the normal state of $(Fe_{1-x}Cu_x)Se_{1-\delta}$ at 15 K, where the linewidth increases rapidly upon Cu doping and then saturates. This implies that Cu substitution induces a magnetic moment so that the line broadening is dominated by magnetic disorder, rather

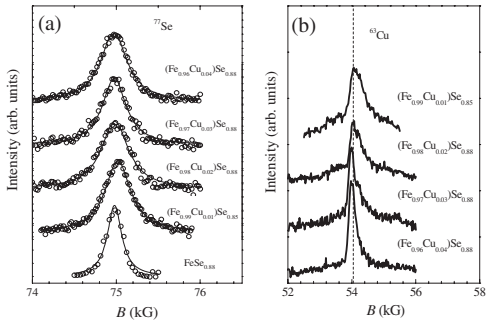

FIG. 8. (a) ^{77}Se and (b) ^{63}Cu NMR spectra, in the normal state of $(Fe_{1-x}Cu_x)Se_{1-\delta}$, at 15 K and 60.99 MHz. Dashed line: the reference field for the unshifted ^{63}Cu nucleus.

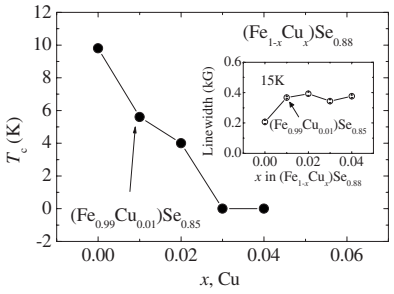

FIG. 9. Superconducting phase diagram of the Cu-doped FeSe. Inset: ^{77}Se NMR linewidth, as a function of Cu doping, at 15 K.

than by structural disorder. Judging by the rapid increase in the ^{77}Se NMR linewidth, the disorder effects may or may not correlate with the rapid suppression of T_c by the Cu doping. In contrast, the ^{63}Cu linewidth [Fig. 8(b)] gradually decreases with the Cu doping, which suggests that the induced moments are not at the Cu sites but at Fe sites.

So why do ^{63}Cu and ^{77}Se linewidths behave so differently? Normally the NMR spectrum becomes wider and more asymmetric when the increase in doping level is begun.[16,17] But here, the ^{63}Cu linewidth can come from both the doping-induced magnetic shift distribution, and the powder patterns due to the anisotropic shifts and quadrupolar effects. The broad shoulders, on both sides of the central peak, are caused by the quadrupolar broadening. Because these broad shoulders stay nearly unchanged, unlike the central peak which sharpens at higher Cu doping, the quadrupolar effects probably do not cause the narrowing of the central peak. Note that the centroid of the spectrum moves closer to the unshifted reference line at higher Cu doping, which implies that the Cu nuclei do not much feel the hyperfine fields, from the neighboring Fe/Cu spins, at a higher doping levels. Since there is no direct chemical bonding between the Cu and Fe atoms, part of the ^{63}Cu frequency shift at low Cu doping comes from the transferred hyperfine coupling, mediated by the conduction electrons. For higher Cu doping, we suspect that the metal-insulator transition reduces the number of conduction electrons so that the transferred hyperfine coupling becomes weaker. Therefore, both the magnetic shift and linewidth decrease at higher Cu doping. This is different from the ^{77}Se spectra, where there is direct wave-function overlap between the Se 4*p* and Fe 3*d* electrons so that the ^{77}Se nucleus can always effectively probe the Fe spins, to show a broader linewidth at higher doping (Fig. 9).

As with Se-deficient FeSe, stretched exponential behavior is observed in the spin-lattice relaxation curves for all $(Fe_{1-x}Cu_x)Se_{1-\delta}$. Their average $(T_1T)^{-1}$ curves are plotted in Fig. 6. Within experimental error, all of our samples show similar average $1/(T_1T)$ behavior, the values increasing at lower temperature. Interestingly, Cu substitution does not alter spin fluctuation in $FeSe_{0.88}$, though Cu^{2+} possesses a spin different from Fe^{2+}. We note that both superconducting volume fraction and T_c rapidly decreases, upon Cu doping. This is different from the Se-deficient samples, where only superconducting volume fraction reduces significantly. The similar superconducting volume fraction, found in $(Fe_{0.99}Cu_{0.01})Se_{0.85}$ and $(Fe_{0.98}Cu_{0.02})Se_{0.88}$, could be an effect of compensation, due to the different values of x and δ. Recent transport experiments, on $(Fe_{1-x}Cu_x)Se_{1-\delta}$, have shown that increasing Cu doping migrates the metallic state to a Mott insulator.[11,12] Therefore, we suspect that the suppression of T_c is mainly due to the change in the electronic states rather than the spin dynamics.

In summary, we conducted comprehensive studies of the ^{77}Si NMR in the Se-deficient and Cu-substituted FeSe. By comparing our data with previous literature, we infer that $FeSe_{1-\delta}$ has an inhomogeneous phase, where the superconductivity emerges from regions with little or no Se vacancy. As for the T_c suppression in $(Fe_{1-x}Cu_x)Se_{1-\delta}$, magnetic fluctuations are not directly relevant. We suspect that it is the electronic states that change most with Cu substitution so that a metal-insulator transition arises after T_c is suppressed.

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