NMR Study of the Dimerized State in $CuIr_2S_4$

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We have investigated the metal-insulator transition (MIT) of $CuIr_2S_4$ by a high resolution NMR measurement. The Cu-NMR spectrum below T_{MI} is broadened and split into four Cu signals with sizable electric quadrupole interactions. The NMR results are consistent with the charge ordering of Ir^{3+} and Ir^{4+} and the spin dimerization of Ir^{4+} spins, as revealed by a recent X-ray study.

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I. INTRODUCTION

In calcogenide spinel $CuIr_2S_4$, the metal-insulator transition (MIT) at T_{MI} ∼230 K [1] has attracted much attention. Since NMR [2] and photoemission [3] measurements show that the Cu ions are monovalent in the insulating state and thus the nominal valence of the Ir atoms is 3.5, the nonmagnetic ground state below T_{MI} is puzzling for possible Ir^{3+} (S=0) and Ir^{4+} (S=1/2) configurations. There are discussions about the charge order of Ir^{3+} (S=0) and Ir^{4+} (S=1/2) ions, and consequently possible spin singlet dimers in the insulating state. This MIT is accompanied by a structural transition from cubic to tetragonal (triclinic) symmetry with volume contraction of 0.7%. [4] Recently, a precise X-ray measurement [5] has shown that a charge ordering of Ir^{3+} and Ir^{4+} and spin dimerization of Ir^{4+} ions occurs simultaneously below T_{MI}. The Ir sublattice consists of two type of Ir bi-capped hexagonal rings which described as Ir^{3+} and Ir^{4+} octamers. In order to elucidate the origin of the MIT in the Cu-spinels, it is important to accumulate the information about the valence state and magnetic properties in the insulating state from a microscopic point of view. Here, we investigate the evolution of the electronic state associated with MIT of $CuIr_2S_4$ by a Cu-NMR study using a high resolution NMR spectroscopy.

II. EXPERIMENTAL

Polycrystalline samples were prepared by solid state reaction [1]. NMR was measured by the conventional phase coherent pulse method with a highly-homogeneous superconducting magnet. Spectra of ^{63}Cu were obtained by the Fourier Transformed-NMR with a constant magnetic field (H=9.4T).

III. RESULTS AND DISCUSSION

As shown in Fig. 1. we obtained very narrow ^{63}Cu spectra above T_{MI} in $CuIr_2S_4$. The line width is less than 5 kHz without any notable anisotropic Knight shift and nuclear quadrupole interactions. The ^{63}Cu NMR spectrum becomes broad below T_{MI}, and shows several peaks within the narrow range of 100 kHz. As the MIT is of a first order transition [1], NMR signals in the metallic and insulating phase coexist for between 230K and 220K. The isotropic part of the Knight shift of ∼ -0.08% at the metallic state indicates that there exists a negative contribution of the Knight shift from core polarizations of the Cu 3d electrons. Below T_{MI}, the opening of a band gap reduces the Knight shift. The absence of apparent temperature dependence of the Knight shift below T_{MI} indicates that the electronic state is basically nonmagnetic in the insulating state, suggesting that both Cu and the Ir atoms in $CuIr_2S_4$ are in nonmagnetic states.

Because of the lattice distortion from cubic to triclinic symmetry below T_{MI}, an appreciable electric field gradient (EFG) at the Cu site is expected. Thus, the nuclear quadrupole interaction for the Cu nuclei (I=3/2) is not negligible below T_{MI}. We have calculated the EFG at the Cu site with a point charge model. For this purpose, we use atomic positions and ionic configurations of Ir^{3+} and Ir^{4+} obtained by the recent precise X- ray measurement. [6] The calculation reveals that only one equivalent Cu site in the cubic symmetry above T_{MI} changes to 4 non equivalent Cu sites. The calculated parameters of V_{zz}, and η are given in Table 1. The number of the Cu sites correspond to the ones assigned in [5].

We simulate the split spectrum by taking into consideration the perturbation of the nuclear quadrupole interaction for the Zeeman field. The best fitting is achieved with superposition of 4 components of the spectrum with the slightly-different Knight shift as shown in Fig. 2. The NMR parameters for the best fittings are listed in Table 2. From the differences of the quadrupole frequency, ν_Q, and anisotropy parameter, η, we assign each NMR component to the signal from the Cu atoms defined in [5]. As seen in Fig. 2, the fitting to the experimental data is satisfactory. This indicates that the charge separation and the possible dimerization of Ir^{4+} proposed by X-ray study are reasonably confirmed by the NMR study at a microscopic point view.

	Cu(1)	Cu(2)	Cu(3)	Cu(4)
V_{zz}^{cal}	4.23	2.27	2.31	3.43
η^{cal}	0.34	0.85	0.74	0.93

TABLE I: Calculated EFG parameters of insulating state in $CuIr_2S_4$.

	line(1)	line(2)	line(3)	line(4)
K^{iso} (%)	0.12	0.104	0.09	0.13
ν_Q (kHz)	88	26	14	89
η	0.34	0.86	0.74	0.92

TABLE II: Fitting parameters of NMR shift and nuclear quadrupole interactions.

Finally, we show the nuclear spin lattice relaxation time, T_1, of ^{63}Cu in Fig. 3. At the metallic state above T_{MI}, $(T_1T)^{-1}$ obeys the Korringa relation (temperature-independent), and decreases largely at T_{MI} due to the opening of the band gap in the insulating state. An interesting feature is that the temperature dependence of $(T_1T)^{-1}$ obeys a power law (the T^2 -relation) and not a thermally activated (exponential relation) behavior. This result indicates that the band gap in the insulating state of $CuIr_2S_4$ is quite anisotropic or that spin fluctuations are in very unusual nature.

IV. SUMMARY

We have investigated ^{63}Cu-NMR in $CuIr_2S_4$. ^{63}Cu-NMR spectrum consists of 4 components of non equivalent Cu-NMR signals with different Knight shift and nuclear quadrupole interaction in the insulating state. The charge ordering of the Ir^{3+} and Ir^{4+} and the dimerization of Ir^{4+} spins in $CuIr_2S_4$ are verified by the NMR study.

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[1] S. Nagata, T. Hagino, Y. Seki, T. Bitoh, Physica **B194-196** (1994) 1077, T. Hagino, T. Tojo, T. Atake and S. Nagata, Philos. Mag. **B71** (1995) 881.
[2] K. Kumagai, S. Tsuji, T. Hagino, S. Nagata, *Spectroscopy of Mott Insulator and Correlated Metals*, eds. by A. Fujimori and Y. Tokura, (Springer-Verlag, 1995) p255.
[3] J. Matsuno, T. Mizokawa, A. Fujimori, D.A. Zatsepin, V.R. Galakhov, E.Z. Kurmaev, Y. Kato, S. Nagata,, Phys. Rev. **B55** (1997) R15979.
[4] T. Furubayashi, T. Matsumoto, T. Hagino and S. Nagata, J. Phys. Soc. Jpn. **63** (1994) 3333.
[5] P. G. Radaelli, Y. Horibe, M.J. Gutmann, H. Ishibashi, C.H. Chen, R.M. Ibberson, Y. Koyama, Y. S. Hor, V. Kiryukhin, S.W. Cheong, Nature **416** (2002) 155.
[6] Y. Horibe, Private communication.

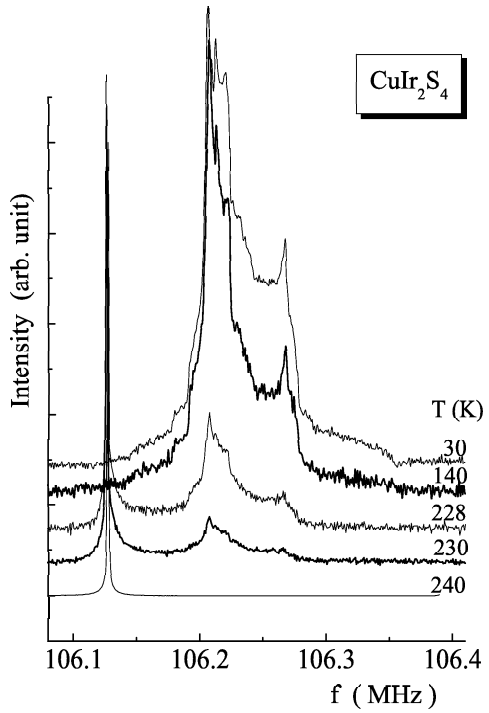

FIG. 1: ^{63}Cu-NMR spectra of $CuIr_2S_4$ at various temperatures. The spectra at T=230 K and T=140 K are shown by bold lines.

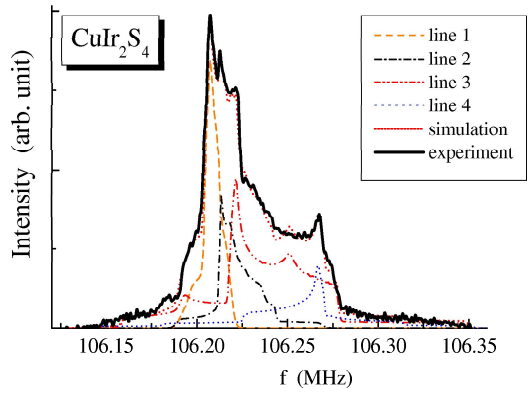

FIG. 2: ^{63}Cu-NMR spectrum of $CuIr_2S_4$ at T=100K. Simulated spectrum which is summed up with NMR lines with reasonable values of quadrupole frequency and Knight shift for inequivalent Cu site are shown.

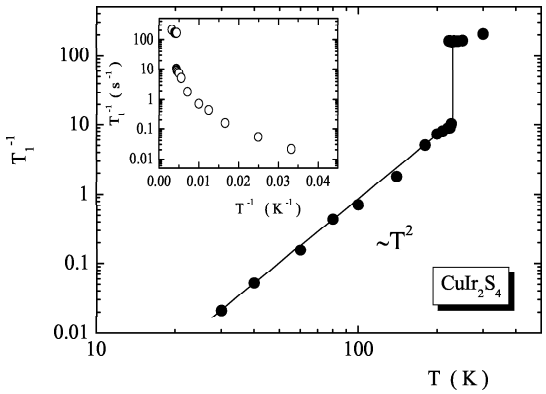

FIG. 3: Temperature dependence of nuclear spin-lattice relaxation rate, $(T_1T)^{-1}$ in $CuIr_2S_4$. The inset shows the T_1^{-1} as a function of T^{-1}.