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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.

keywords: NMR, metal-insulator transition, spinel, CuIr_2S_4

PACS numbers:

I. INTRODUCTION

In calcogenide spinel CuIr_2S_4 , the metal-insulator transition (MIT) at $T_{MI} \sim 230$ 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 ($H=9.4\text{T}$).

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 $\sim -0.08\%$ 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 non-magnetic 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 in-

teresting 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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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 $T=100$ K. 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} .