NMR investigation of a structural phase transition and temperature-induced magnetism in copper thiospinel CuV_2S_4

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Metallic thiospinel CuV_2S_4 transforms from the high-T cubic (HTC) crystal phase to a low-T tetragonal (LTT) phase below a transition temperature $T_f=90$ K. The electronic and magnetic properties of CuV_2S_4 have been investigated with magnetic susceptibility χ, Knight shift K, and nuclear spin-lattice relaxation time T_1 measurements between $T=4.2$ and 300 K at 78 MHz. With the phase transition from HTC to LTT, the d-spin hyperfine field of ^{51}V shows a large change from -29.4 to 2.5 kOe/μ_B and of ^{63}Cu from 19.5 to 11.9 kOe/μ_B. The small increase in χ and large increase in K^2T_1T above T_f are described by an energy band scheme of V^{3+} (d^2) with a singlet ground state ($S=0$) and triplet first-excited state ($S=1$). A large Jahn-Teller local distortion in the LTT phase results in the singlet ground state. In the HTC phase, on the other hand, the distortion is so small as to allow a thermal excitation to the triplet state with an activation energy of $\Delta E\simeq 13$ meV. [S0163-1829(97)04802-9]

INTRODUCTION

Diverse electronic and magnetic properties emerging from spinel compounds AB_2X_4 when various atoms of A, B, and X are combined have been extensively studied in the past few decades. Above all, there has been a renewed interest in the superconducting copper spinel CuM_2X_4 in which the Cu atoms are in the Cu^{2+} ionic state[1–4] as the case of cuprate *high*-T_c superconductors.

In CuV_2S_4, contrary to the early discovery of the superconductivity with $T_s=3.95$–4.45 K,[5] none of following reports[6–11] showed any sign of the superconductivity, and the recent studies[6,8,9] on CuV_2S_4 have been focused on the subject of charge density wave (CDW) formation to explain an anomalous resistivity maximum around 50 K.[7,11] Nuclear magnetic resonance (NMR) studies[7,10] found that a negative Knight shift of ^{51}V in CuV_2S_4 becomes significantly weaker below ~90 K. This was explained to be associated with a partial quenching of the Fermi surface due to the CDW formation.[10]

Because of the topology of the Fermi surface, the Peierls transition and resulting CDW formation is well known to be a general property of one-dimensional (1D) conducting systems, and to be rare in 3D conductors with cubic structure.[12] In addition, Miyatani, Tanaka, and Miyamoto[13] showed by x-ray diffraction (XRD) measurements that a well-characterized stoichiometric CuV_2S_4 specimen exhibits a coherent-type crystal-phase transition from the high-T cubic (HTC) to a low-T tetragonal (LTT) at $T_f=90$ K. Thus CuV_2S_4 is restudied here, using the well-defined stoichiometric sample.

In this paper, we report briefly the experimental results and analysis of the magnetic susceptibility and high-field NMR study of both ^{63}Cu and ^{51}V in the metallic CuV_2S_4. The results are well described by an energy band scheme of V^{3+} (d^2) with a singlet ground state ($S=0$) and triplet first-excited state ($S=1$). In the HTC phase, the energy separation between the two states is so small as to allow the thermal excitation.

EXPERIMENT

A polycrystalline specimen used in the present study was synthesized by the standard shielded ampoule method. The dependence of the lattice parameters on T determined by the powder XRD (Ref. 13) is shown in Fig. 1, where c/a is

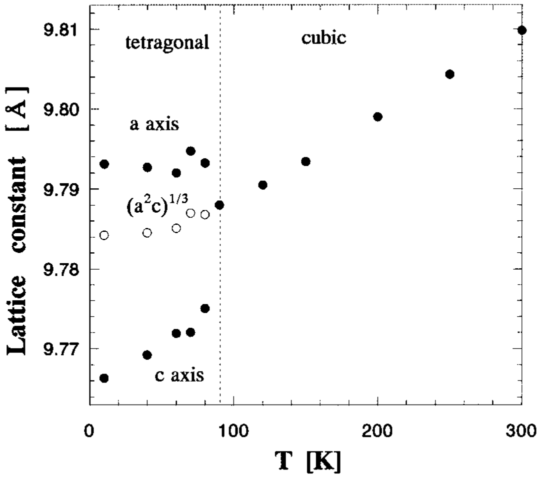

FIG. 1. Temperature dependence of the lattice parameters by Miyatani, Tanaka, and Miyamoto (Ref. 13).

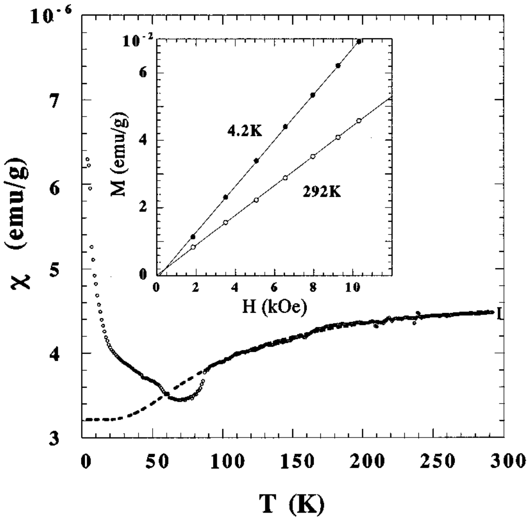

FIG. 2. Temperature dependence of the magnetic susceptibility χ. Broken curve shows the temperature-induced χ discussed in the text. Inset shows a typical field dependence of the magnetization at 4.2 and at 292 K.

about 0.9975 for $T<60$ K. Thus the HTC spinel CuV_2S_4 coherently transforms into the LTT spinel below $T_f=90$ K.

The magnetization M measured in a T range between 4.2 and 300 K using a torsion-type magnetic balance was proportional to the external field H (inset of Fig. 2). Thus the slope dM/dH could be described by the susceptibility χ. As shown in Fig. 2, χ shows a characteristic T dependence as reported previously;[7] with decreasing T, a small decrease in the T range between 90 and 300 K, sudden decrease just below 90 K and large increase below ~60 K.

NMR of both ^{63}Cu ($I=\frac{3}{2}$) and ^{51}V ($I=\frac{7}{2}$) was observed in the T range between 4.2 and 300 K using a phase-coherent spin-echo spectrometer operating at 78 MHz. The ^{63}Cu NMR for $T<90$ K was observed in the present study. As shown in Fig. 3, the linewidth of both ^{63}Cu and ^{51}V with a Lorentzian line shape at high T exhibits a monotonic increase at low T with a small anisotropic shape. The linewidth of ^{51}V shows, in addition, a significant increase for T from ~150 K down to 90 K.

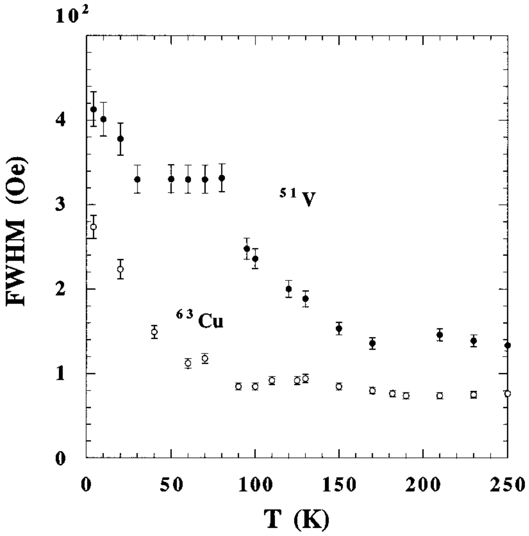

FIG. 3. Temperature dependence of the full-width of half maximum (FWHM) of the ^{63}Cu and ^{51}V resonance line.

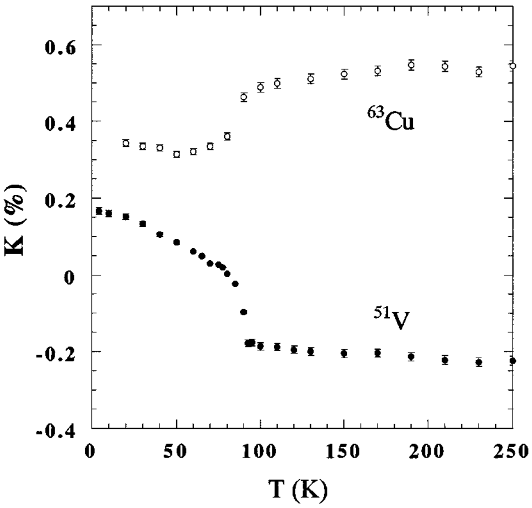

FIG. 4. Temperature dependence of the Knight shift K.

Figure 4 shows the T dependence of the Knight shift K. The data of ^{63}K above 90 K and of ^{51}K agree with the values reported previously.[7,10,14] Shown in Fig. 5 is the K vs χ plot with T the implicit parameter.

The Knight shift in CuV_2S_4 has contributions coming mainly from s spin, d spin, and d orbital, neglecting the diamagnetic contribution,

$$K=K_s+K_d(T)+K_{\rm orb}, \tag{1}$$

and these, in turn, are related to the susceptibilities with hyperfine coupling constants by

$$K_s=(\gamma_e\gamma_N\hbar^2)^{-1}A_s\chi_s, \tag{2}$$

$$K_d=(\gamma_e\gamma_N\hbar^2)^{-1}A_d\chi_d, \tag{3}$$

$$K_{\rm orb}=(\gamma_e\gamma_N\hbar^2)^{-1}A_{\rm orb}\chi_{\rm orb}, \tag{4}$$

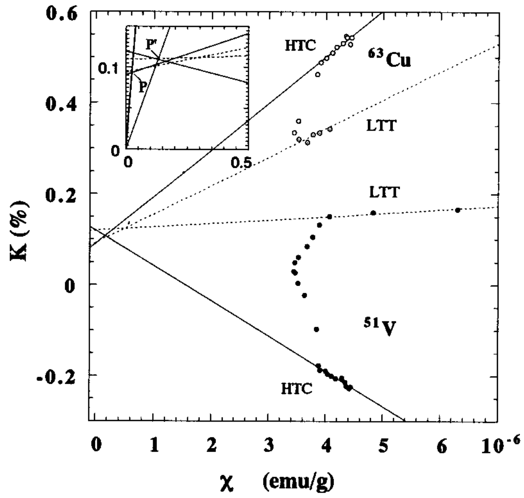

FIG. 5. Plot of the Knight shift K against the susceptibility χ.

where A_d includes the core polarization (A_{cp}), dipolar (A_{dip}), and spin-orbit (A_{so}) contribution.[15]

HTC phase. The experimental data of both ^{63}Cu and ^{51}V for $T>90$ K are on a corresponding solid line drawn in Fig. 5 using a least-squares method. The slope of the experimental K vs χ line yields an empirical value for A_d; 19.5 and -29.4 kOe/μ_B for ^{63}Cu and ^{51}V, respectively. The negative sign of $^{51}A_d$ is indicative of dominant d spin contributions. The positive sign of $^{63}A_d$, in contrast, is suggestive of dominant transferred hyperfine couplings $^{63}B_{\text{tr}}$ to the neighboring V d spins through four nearest-neighbor sulfur atoms. Thus we estimate $^{63}B_{\text{tr}} \simeq 3.0$ kOe/μ_B.

An intersection (at point P for ^{63}Cu and P' for ^{51}V in the inset of Fig. 5) of the experimental K vs χ line and K_{orb} vs χ_{orb} line with the slope defined by A_{orb} gives an estimate of K_{orb} and χ_{orb}, neglecting a small contribution from the s band in CuV$_2$S$_4$.[7,16] Taking $^{51}A_{\text{orb}}=322$ kOe/μ_B and $^{63}A_{\text{orb}}=745$ kOe/μ_B (Ref. 17) and a typical reduction factor $k=0.8$ in metals, we obtained $^{51}K_{\text{orb}} \simeq 0.11\%$, $\chi_{\text{orb}} \simeq 0.13 \times 10^{-6}$ emu/g V$_2$ and $^{63}K_{\text{orb}} \simeq 0.1\%$, $\chi_{\text{orb}} \simeq 0.02 \times 10^{-6}$ emu/g Cu, respectively. Thus we may conclude that the experimental large χ of $\sim 3 \times 10^{-6}$ emu/g is mainly attributed to the V d spins at the B site.

LTT phase. As the system transforms into the LTT phase just below 90 K, the experimental points deviate remarkably from the extrapolation of the K vs χ line defined in the HTC phase (solid line), and then are on another line with different slope (broken line) at low T for the case of both ^{63}Cu and ^{51}V. The experimental fact that the extrapolation of the broken line reaches the point P (P') leads us to conclude that, associating with the phase transition from the HTC to LTT phase, (1) the orbital contribution to K and to χ does not change and (2) the value of the d spin hyperfine coupling constant A_s varies from -29.4 to 2.5 kOe/μ_B for ^{51}V and from 19.5 to 11.9 kOe/μ_B for ^{63}Cu, respectively.

The nuclear spin-lattice relaxation rate T_1^{-1} was measured utilizing the single-rf-pulse–saturation method. All the experimental magnetization $M(t)$ at the time t after the single-saturation pulse showed a multiexponential recovery, and T_1 was obtained by the parameter fitting of the theoretical recovery curve with the experimental data.[3] T_1^{-1} shown in Fig. 6 exhibits characteristic T dependences at $T \sim 90$ K: i.e., a jump discontinuity in $^{51}T_1^{-1}$ and a maximum in $^{63}T_1^{-1}$. These behaviors would naturally be affected by the unexpected change in the value of the d spin hyperfine coupling A_d. In Fig. 7 we plot the value of $K_d^2 T_1 T$ against T with A_d the implicit parameter. A roughly T independent behavior of $K_d^2 T_1 T$ for $T<90$ K indicates that the very large increase in χ below ~ 60 K is attributed to an increase in effective density of states (DOS) at the Fermi level E_F, expected when the V d band width is extremely narrow ($\lesssim 100$ K). The large increase in $K_d^2 T_1 T$ for $T>90$ K, on the other hand, indicates that the increase in χ for $T>90$ K (Fig. 2) cannot simply be explained by the increase in DOS at E_F.

DISCUSSION

Anomalies in the conductivity and magnetic susceptibility observed in CuV$_2$S$_4$ have been interpreted as a sign of the CDW formation in previous papers. Present experimental results on the Knight shift and relaxation rate of both ^{63}Cu and ^{51}V, however, could not be explained by the occurrence of the Peierls transition. The XRD study[13] (Fig. 1) exhibits evidence not for the superlattice diffraction pattern due to the CDW formation, but for the structural transition from the HTC phase to LTT phase at $T_f=90$ K.

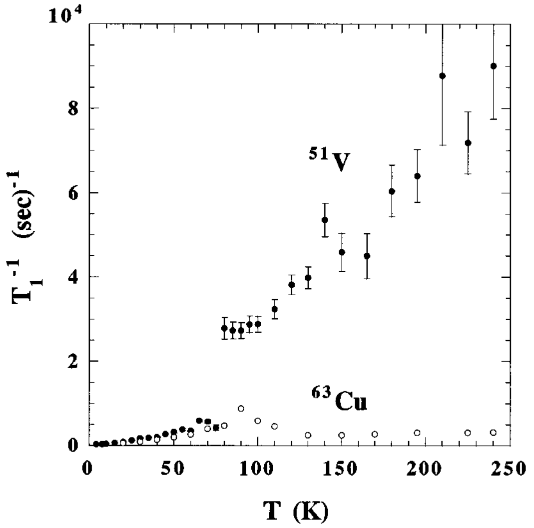

FIG. 6. Temperature dependence of the nuclear spin-lattice relaxation rate $(T_1)^{-1}$.

Some transitional compounds (oxides, sulphides, selenides, tellurides) with metallic conductivity are known to retain large ionic character. Following the strong crystal field theory, the ground state of the electron configuration in the cubic CuV$_2$S$_4$ spinel is expected to be in an ion distribution given by Cu^{2+}(V^{3+})$_2$(S^{2-})$_4$ with $(e_g)^4(t_{2g})^5$ for Cu^{2+} at the tetrahedral A site and $(t_{2g})^2$ for V^{3+} at the octahedral B site. The triply degenerate $(t_{2g})^2$ electron configuration ($S=1$, $L=3$) of V^{3+} should give rise to a Curie-Weiss-type spin susceptibility, which is not the present case of CuV$_2$S$_4$.

When the crystal is distorted ($c<a$), the t_{2g} orbital splits into a nondegenerate ground state of d_{xy} orbital and doubly degenerate excited state of d_{xz} and d_{yz} orbital. The Jahn-

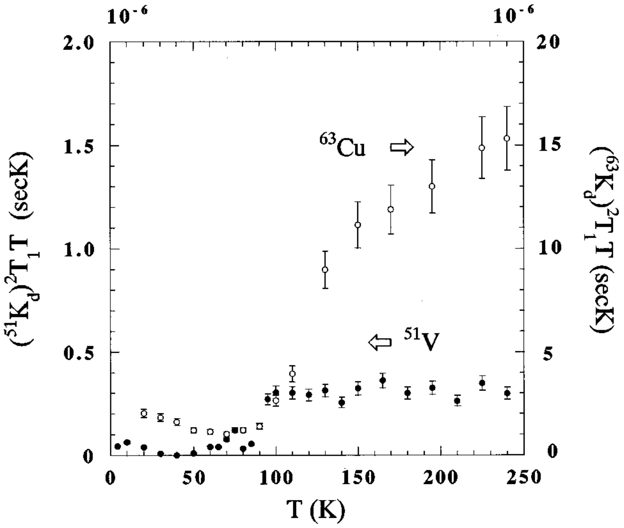

FIG. 7. Plot of $K_d^2 T_1 T$ against the temperature.

Teller local distortion along the c axis at the B site results in a singlet ground state ($S=0$, $L=0$), and the $S=1$ triplet state is expected to be induced by thermal excitations as T is raised. The increase in the ^{51}V linewidth observed in the T range from ~150 down to 90 K (Fig. 3) would be due to the quadrupole broadening associated with the growth of the local distortion at the B site.

A statistical calculation of χ_s for two electrons in a system composed of the spin-singlet ground state and spin-triplet excited state gives

$$\chi \propto \frac{e^{-\Delta E/k_B T}(2+e^{-\Delta E/k_B T})}{(1+e^{-\Delta E/k_B T})^2}. \tag{5}$$

The data of χ for $T>90$ K are satisfactorily reproduced by a broken curve drawn in Fig. 2 using Eq. (5) with $\Delta E \sim 150$ K ($\simeq 13$ meV).

Thus we may conclude that, in the HTC phase, the Jahn-Teller local small distortion at the B site gives the low-lying excited state ($\Delta E \sim 13$ meV) of spin triplet ($S=1$) to allow the thermal excitation from the spin-singlet ground state. The influence of the d-d Coulomb correlations would lead to a screening out of the short-range repulsive potential between the electrons with antiparallel spin direction.

The experimental χ just below $T_f=90$ K deviates from the broken curve and decreases suddenly. This indicates that, in the LTT phase, the energy separation between the singlet ground state and triplet excited state becomes large enough not to allow the thermal excitation. The roughly T independent behavior of $(^{51}K)^2 T_1 T$ for $T<90$ K also suggests that the electronic state in the LTT phase is in the singlet ground state.

Finally, the positive sign of $^{63}A_d$ implies that the electronic state of the Cu atom at the A site is in a state close to Cu^{1+} ($d^{10}, S=0$). Further detailed analysis of the experimental results will be reported in the near future.

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