Powder Spectra of ^{51}V NMR in CuV_2S_4: Possible Coexistence of Charge and Spin Density Waves*

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NMR experiments are reported for the copper chalcogenide spinel CuV_2S_4, which has incommensurate lattice distortions at low temperatures in spite of the cubic symmetry at high temperature. A broad spin-echo spectrum of ^{51}V has been observed below 90 K at 17 MHz, but it shows a remarkable frequency dependence where it becomes sharper with decreasing frequency. Possible coexistence of charge and spin density waves is suggested at low temperatures in this material.

Key words: NMR, CDW, SDW, chalcogenide, spinel.

1. Introduction

The ternary thiospinel CuV_2S_4 has the normal cubic spinel structure at room temperature, where Cu atoms occupy the tetrahedral A sites and V atoms occupy the octahedral B sites as shown in Figure 1.

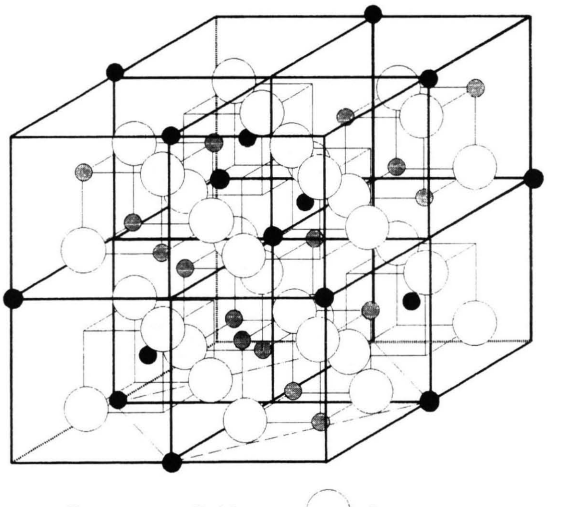

Fig. 1. Crystal structure of CuV_2S_4. Copper atoms occupy the tetrahedral A sites and Vanadium atoms occupy the octahedral B sites.

It has metallic conductivity and the superconductivity has not been observed above 60 mK [1, 2]. Incommensurate lattice distortions were observed by X-ray diffraction at low temperatures. They are considered to be due to the formation of charge density waves (CDW's): A CDW forms with a reduced wave vector $\boldsymbol{q} = (1/4 - \mathrm{d})$ [110] at 90 K [3]. The incommensurability d decreases with decreasing temperature, and lock-in (d = 0) occurs at 75 K [3]. At about 50 K a first order transition to a new incommensurate CDW structure with $\boldsymbol{q} = (1/3)$ [110] occurs [3]. A somewhat different structure model was proposed from the analysis of an electron diffraction study: A domain structure consisting of six orientation variants, corresponding to symmetry lowering from cubic to orthorhombic was proposed [4]. Incommensurate reflections lead to a structure model consisting of quasi-periodically stacked antiphase boundaries characterized by a displacement vector (1/2) [101], [4]. The deformation modulation was interpreted in terms of dimerized ⟨110⟩ types of copper-atom zig-zag chains [4]. Since the formation of the incommensurate CDW is quite rare in the three dimensional systems, CuV_2S_4 seems to be the first example of incommensurate CDW for compounds with spinel structure. A Jahn-Teller distortion may occur in the octahedral Cu sites, but there is no simple reason for the onset of the incommensurate wave in the copper spinels. Thus, we planned to investigate the incommensurate CDW states in CuV_2S_4 from a microscopic point of view by means of pulsed NMR techniques.

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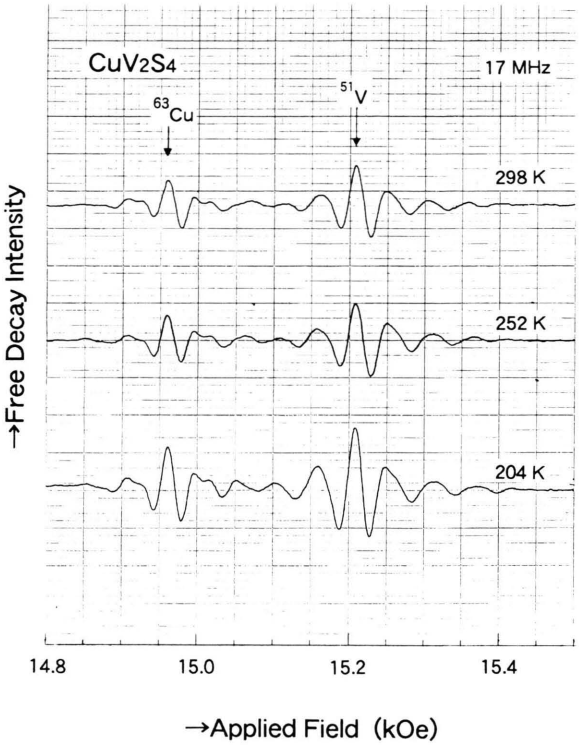

Fig. 2. Examples of free-decay wiggles of ^{51}V and ^{63}Cu NMR at high temperatures in CuV_2S_4.

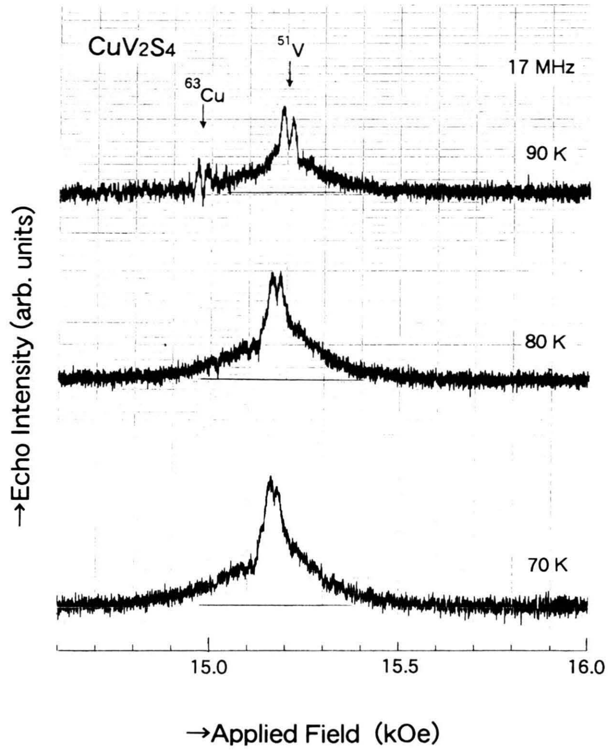

Fig. 3. Examples of spin-echo spectra of ^{51}V NMR below 90 K in CuV_2S_4.

2. Experimental results and discussion

Powder specimens of CuV_2S_4 were obtained in the way described in [2]: Mixtures of high-purity fine powders of Cu, V, and S were heated in sealed quartz tubes at 1073 K for 10 days. The pure spinel phase was confirmed by X-ray diffraction. The NMR experiments have been performed in a temperature range between 4.2 and 300 K with a home-set-up, phase-coherent pulsed NMR spectrometer. Sharp free decay signals of ^{51}V and ^{63}Cu have been observed above 90 K. Examples are shown in Figure 2. Below 90k, both resonances show a drastic change. Examples of spin-echo spectra are shown in Figure 3. At 90 K the free decay signal of ^{63}Cu has disappeared and that of ^{51}V has lost most of its intensity. New broad spin-echo signals appear below 90 K as are seen in the figure. The temperature dependence of the relative intensity of the signals of ^{51}V and ^{63}Cu is shown in Fig. 4, and the temperature dependence of the shifts of the resonances of ^{51}V and ^{63}Cu is plotted in Figure 5. The latter is in good agreement with continuous wave NMR experiments reported previously [5]. The broad

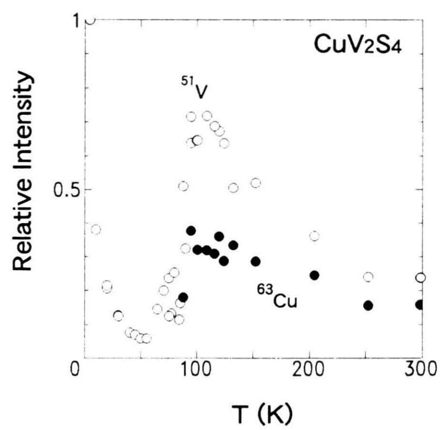

Fig. 4. Temperature dependence of relative intensity of ^{51}V and ^{63}Cu NMR in CuV_2S_4.

spin-echo signals below 90 K in Fig. 3 are considered to be powder spectra of NMR perturbed by nuclear quadrupole interaction for $I = 7/2$, but the satellite transitions are not very clear. we examined the frequency dependence of the powder spectrum and found a very remarkable effect, i. e., the satellite transitions

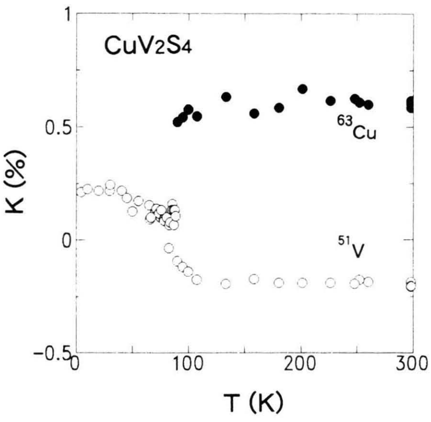

Fig. 5. Temperature dependence of the shifts of the resonances of ^{51}V and ^{63}Cu in CuV_2S_4.

become sharper with decreasing frequency. An example at 4.2 K is shown in Figure 6. This seems to be the first example where such an effect has been observed. This effect can be interpreted if the principal axes of the field gradients are different from those of the Knight shift, because there is no reason for the smearing of satellite transitions if both coincide. Actually, rather sharp zero-field NMR spectra in Mn_4N at low temperatures are interpreted by the combined effect of an anisotropic hyperfine field and quadrupole interactions, both of wich have axial symmetries at one of the manganese sites [6]. Therefore, the local symmetries of the charge and the spin density around ^{51}V must be different, providing an indication of the coexistence of CDW and SDW in this material at low temperatures. The rather sharp powder spectrum with ν_Q $(= 3e^2qQ/2I(2I{-}1)h)$ of 208 kHz in Fig. 6(a) in the incommensurate CDW state supports a discommensuration model in which the signals come from locally

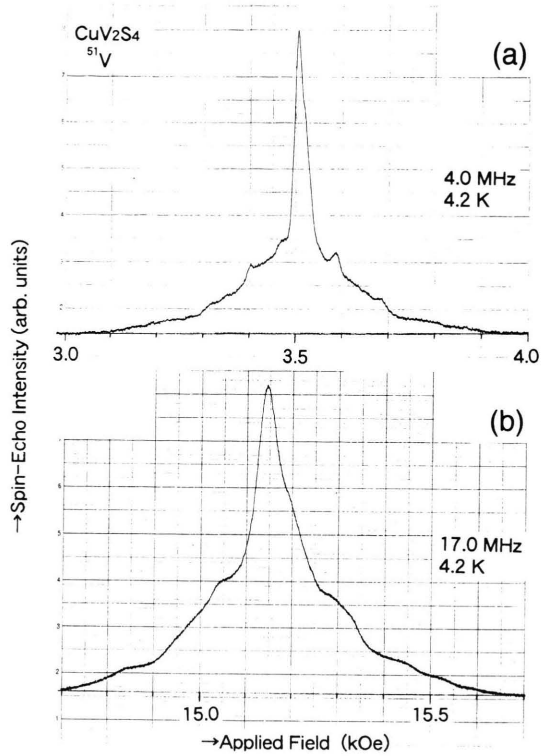

Fig. 6. Boxcar traces of ^{51}V spin-echo NMR at 4.2 K at operating frequencies of 4 MHz (a) and 17 MHz (b) in CuV_2S_4.

commensurate regions separated by regions of phase slip as was observed in cases of layered disulfides [7].

In summary, the broad spin-echo spectrum of ^{51}V observed below 90 K in CuV_2S_4 shows a remarkable frequency dependence where it becomes sharper with decreasing frequency. A possible coexistence of charge and spin density waves is suggested at low temperatures in this material.

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