Change in ^{51}V Relaxation Rates due to CDW in CuV_2S_4 *

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Z. Naturforsch. **51a,** 773–776 (1996); received April 2, 1996

The temperature variations of the ^{63}Cu, ^{65}Cu and ^{51}V NMR spectra and ^{51}V spin-lattice relaxation rate $1/T_1$ have been measured in a thiospinel CuV_2S_4. Drastic changes in the spectra and relaxation rates were observed at the charge density wave (CDW) transition temperature. With decreasing temperature T, $1/T_1$ decreases exponentially due to the CDW transition ($75\ K < T < 90\ K$). The energy gap made by the CDW formation at 90 K is estimated to be 0.052 eV from an Arrhenius plot of $1/T_1$.

Key words: CuV_2S_4, charge density wave (CDW), NMR spectra, spin-lattice relaxation rate, energy gap.

Introduction

Copper sulfide spinels are interesting in connection with the high T_C Cu-oxide superconductors [1, 2]. The compounds $Cu_{1+x}Rh_{2-x}S_4$ are superconducters whose critical temperature is almost independent of x [3]. The system $Cu_{1+x}Co_{2-x}S_4$ reveals an antiferromagnetic phase transition at about 18 K and a superconducting transition at about 2 K depending on x [4]. $CuIr_2S_4$ has a metal-insulator transition at 220 K [5].

The ternary sulfide CuV_2S_4 has a cubic spinel structure at room temperature. Cu ions occupy the tetrahedral A sites which are surrounded by four sulfide ions, while V ions occupy the octahedral B sites which are surrounded by six sulfide ions. Evidence of a charge density wave (CDW) formation has been reported in CuV_2S_4, although the likelihood of a CDW state is small in three-dimensional materials. According to Fleming et al. [6], at 90 K a phase transitioin appears and results in an incommensurate superlattice whose incommensurability smoothly decreases with decreasing temperature and ends up in a commensurate superlattice at 75 K. Below about 50 K another weekly incommensurate superlattice appears again.

We have studied the CDW transition in CuV_2S_4 by measuring ^{63}Cu, ^{65}Cu and ^{51}V NMR. In [7] we showed the apparent temperature-variations of the ^{63}Cu, ^{65}Cu, and ^{51}V NMR spectra, the temperature dependences of the half width $^{63}(\Delta H)$ and $^{51}(\Delta H)$, and those of the Knight shifts ^{63}K of ^{63}Cu, and ^{51}K of ^{51}V. We discussed the sudden changes of these physical quantities at the CDW transition temperatures, and some of their abnormal behavior at high temperatures. The hyperfine coupling constant $^{63}H_{hf}$ was estimated from the $K-\chi$ plot. In this paper we report some NMR spectra and the results of the ^{51}V spin-lattice relaxation measurements.

* Presented at the XIIIth International Symposium on Nuclear Quadrupole Interactions, Providence, Rhode Island, USA, July 23–28, 1995.

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1. Experimental

Polycrystalline CuV_2S_4 was obtained by a conventional vacuum shielded ampoule method. X-ray measurements certified the spinel structure of CuV_2S_4. The sample was crushed into 200-mesh powder.

The NMR measurements between 4.2 and 300 K were made with a conventional phase-coherent spectrometer at 15 MHz. The ^{51}V nuclear spin-lattice relaxation rate $1/T_1$ was measured by recording the variation of the spin-echo intensities against the delayed time t after the inversion π pulse of the $\pi/2-\pi$ pulses.

2. Results and Discussion

The temperature dependence of the ^{63}Cu, ^{65}Cu and ^{51}V NMR spectra has been observed in detail, and some results observed at 4.2 K, 65 K, 87 K and 120 K are shown in Figure 1. As stated in [7], the ^{63}Cu and ^{65}Cu NMR signals disappear suddenly below 83 K

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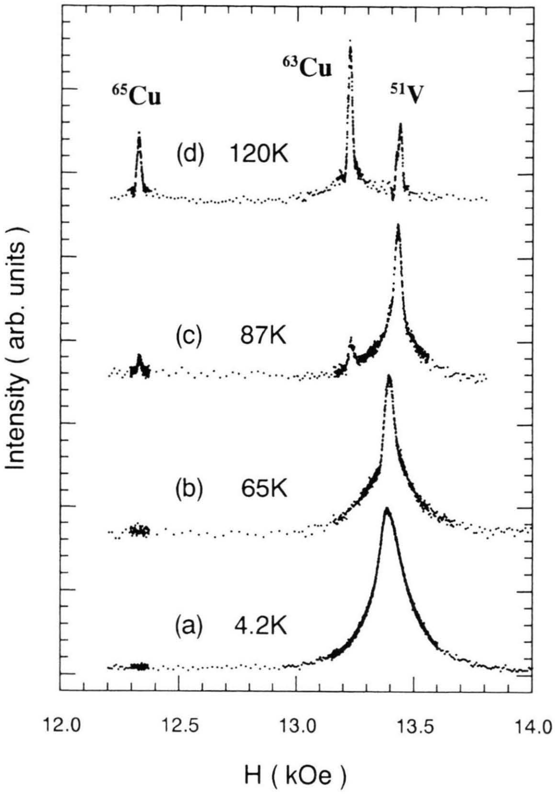

Fig. 1. ^{51}V, ^{63}Cu and ^{65}Cu NMR spectra of CuV_2S_4 at four temperatures.

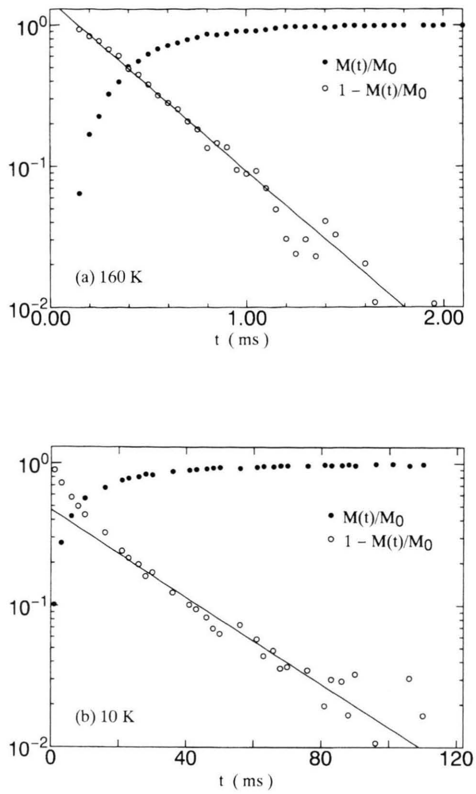

Fig. 2. Recoveries of the ^{51}V nuclear magnetization in CuV_2S_4 at 160 K (a) and 10 K (b).

due to the sudden increase in the electric field gradient (EFG) at the Cu sites caused by the CDW transition [8]. The EFG at the V sites also increased suddenly at the CDW transition temperature. The peak resonance field of ^{51}V NMR, that is the Knight shift ^{51}K of ^{51}V, changes drastically at the CDW transition temperature. Another interesting point is that the ^{51}V NMR intensity is seemingly much smaller than the ^{63}Cu NMR intensity at high temperatures, although in general, the former is much stronger than the latter, and in CuV_2S_4 the number of V nuclei is twice that of Cu nuclei. The origin of this interesting observation is that the spin echo decay of ^{51}V is Lorentzian while that of ^{63}Cu is Gaussian. The extrapolated echo intensities at $\tau = 0$ give a reasonable intensity ratio, where τ is the time interval between the observing $\pi/2$ and π pulses. A detailed discussion will be given in a future paper.

As shown in Fig. 2a the recovery of the ^{51}V nuclear magnetization is single exponential above 100 K. (In Fig. 2a an example observed at 160 K is shown.) However, it is not single-exponential below 100 K, which reflects the increased EFG and the broadened lineshape due to the CDW transition. An example observed at 10 K is shown in Figure 2b. In such a case the estimation of the relaxation rate is not easy. Thus we estimated the longest relaxation time at low temperatures as shown by the solid line in Figure 2b. The obtained relaxation rate $1/T_1$ is plotted against temperature in Figure 3. At high temperatures, $1/T_1$ decreases linearly with decreasing temperature down to 90 K, decreases abruptly below 90 K, and again decreases linearly with temperature below about 70 K. By the least squares fit shown in Fig. 3, we got the Korringa relation $1/T_1T = 17.6\ s^{-1}\ K^{-1}$ ($T > 150$ K), $1/T_1T = 15.5\ s^{-1}\ K^{-1}$ ($100\ K < T < 150$ K) at high temperatures and $1/T_1T = 5.37\ s^{-1}\ K^{-1}$ at low temperatures ($T < 70$ K). There may be some phase transition around 150 K. In the $\chi_0 - T$ curve, a kink is also observed [7]. The density of states of the conduction

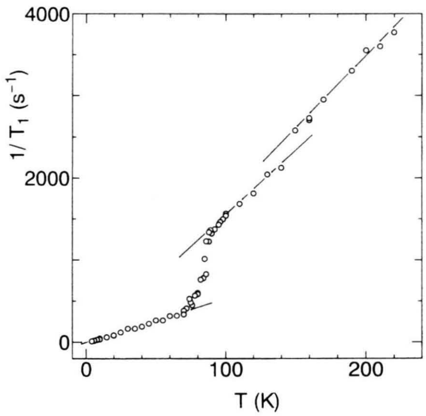

Fig. 3. Relaxation rates $1/T_1$ of ^{51}V in CuV_2S_4 vs. temperature. The lines show the best fitted Korringa relations

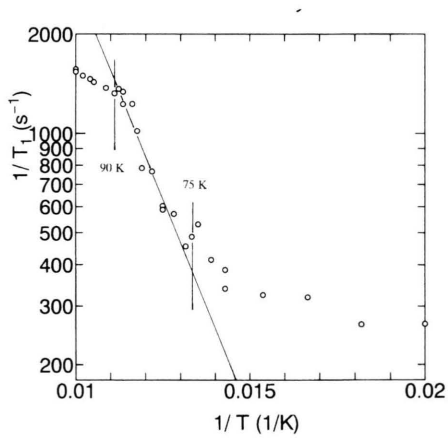

Fig. 4. Arrhenius plot of $1/T_1$ of ^{51}V in CuV_2S_4 between 100 K and 50 K. The best fitted line for $75\ K < T < 90\ K$ gives an energy gap of 0.052 eV.

electrons suddenly decreased to about 60% of that at high temperatures by the CDW formation, although CuV_2S_4 is a three-dimensional compound.

The sudden decrease of $1/T_1$ observed below 90 K is considered to reflect the energy gap formation due to the CDW transition. If an energy gap ΔE is formed at the Fermi level, the spin-lattice relaxation rate $1/T_1$ varies exponentially with temperature T as

$$1/T_1 \propto \exp(-\Delta E/k_B T). \quad (1)$$

The Arrhenius plot of the $1/T_1$ data obtained between 100 and 50 K is given in Figure 4. A good linear relation for the data observed at $75\ K < T < 90\ K$ is obtained, and we can estimate the energy gap to be 0.052 eV by a least squares fit. By the CDW transition, the two 3d electrons with opposite spins are distributed on each wavelength of the CDW and fall into the singlet lower energy state below an energy gap ΔE. This exponential decrease of $1/T_1$ is consistent with the fact that the ^{51}V NMR Knight shift ^{51}K suddenly changes at about 90 K from negative values at high temperatures to positive values at low temperatures, as shown in [7], because the negative Knight shift arises from the core-polarization due to 3d electron spins while the positive Knight shift arises mainly from the Van Vleck orbital moment.

It appears to be another interesting observation that $1/T_1$ is proportional to the temperature below 70 K although the different CDW states are formed even in this temperature range. Further discussions including one about the fast relaxing part will be given elsewhere before long.

3. Conclusion

The variation of the ^{63}Cu, ^{65}Cu, and ^{51}V NMR spectra with temperature has been measured in the thiospinel CuV_2S_4. The ^{63}Cu and ^{65}Cu NMR signals disappear suddenly below 83 K due to the sudden increase of the EFG at the Cu sites caused by the CDW transition. The EFG at the V sites also increases suddenly at the CDW transition temperature. The peak resonance fields of ^{63}Cu, ^{65}Cu, and ^{51}V NMR change drastically at the CDW transition temperature. Both at high temperatures ($T > 100$ K) and at low temperatures ($T < 70$ K), the ^{51}V spin-lattice relaxation rates $1/T_1$ are proportional to the temperature. There seems to be a phase transition at about 150 K. The energy gap made by the CDW formation is estimated to be 0.052 eV by least squares fitting in an Arrhenius plot.

The authors thank Profs. K. Asayama of Osaka University and K. Mizuno of Tokushima University for valuable discussions.

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