NMR of ^{51}V in VRuP: Possible Onset of Charge-Density-Waves*

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NMR experiments are reported for VRuP which has an orthorhombic TiNiSi structure and shows anomalies in the temperature dependence of the electric conductivity and static susceptibility. A field-swept spectrum of ^{51}V perturbed by a quadrupole interaction has been observed, which shows no anomalous temperature dependence. However, the metallic spin-lattice relaxation rate decreases in a stepwise fashion with decreasing temperature at around 200 K, in accordance with the resistivity and the susceptibility data, suggesting a possible CDW formation in this material.

Key words: NMR; CDW; VRuP; ^{51}V; Spin-Lattice Relaxation.

1. Introduction

The compounds MRuP (M = 3 d transition metal) have either the hexagonal Fe_2P or the orthorhombic TiNiSi structure and show interesting magnetic and conduction properties for studying electron-electron correlation in narrow d-bands [1]. FeRuP is an itinerant ferromagnet with Curie temperature of 184 K [2], and MnRuP is an insulating antiferromagnet at low temperatures [3]. The new compound VRuP has the orthorhombic TiNiSi structure, as is shown in Fig. 1, where the projection of atom positions on the $a-c$-plane is depicted. Each vanadium atom is situated in a pyramid formed by five phosphorus atoms. The pyramids are connected by edge-sharing to form a two-dimensional zigzag network along the $a-b$-plane which is shown with thin broken lines in the figure. If the interaction along the zigzag network is strong, the electronic system is considered to be quasi-two-dimensional,while it could be three-dimensional if the interaction between vanadium atoms via apex phosphorus is strong. The compound VRuP was originally thought to be a simple Pauli-paramagnet, however, it is found to have anomalies in the temperature dependence of the electric conductivity and the static susceptibility at around 200 and 270 K. We try to see the change of the electronic state from a microscopic viewpoint by doing NMR experiments of ^{51}V, since quadrupole interaction for ^{51}V ($I = 7/2$, $Q = -0.04$ barn) is expected to strongly disturb a field-swept NMR spectrum if the local symmetry around V atom is changed by charge-density-wave (CDW) transitions [4].

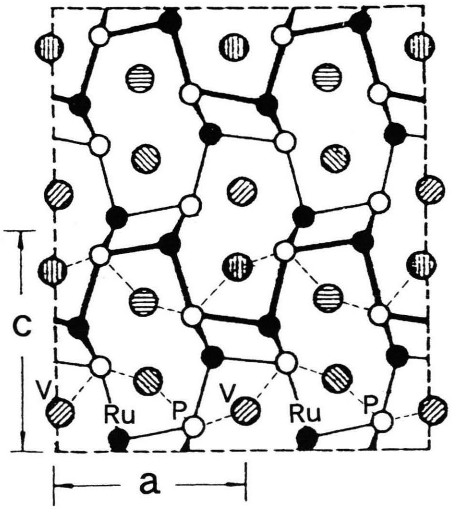

Fig. 1. The crystal structure of VRuP, where the projection of atom positions on the $a-c$-plane is shown. Atoms connected with thick and thin lines are separated by $b/2$ along the b-direction.

2. Resistivity and Static Susceptibility

The powdered sample of VRuP has been synthesized at Tohoku Gakuin University in the following way. Prop-

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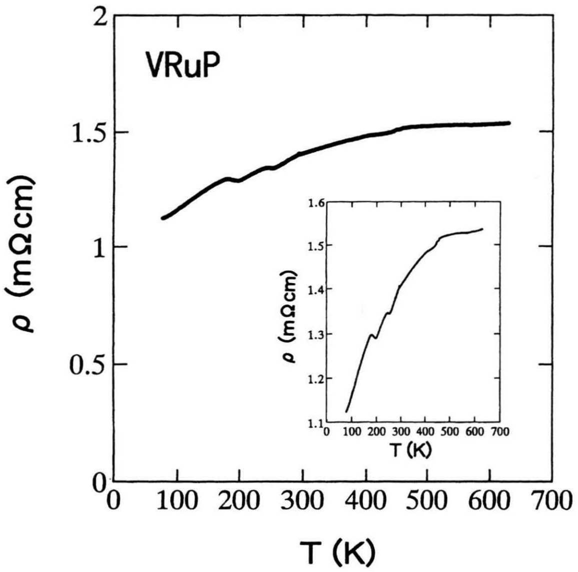

Fig. 2. Temperature dependence of the electric resistivity for a sintered sample of VRuP.

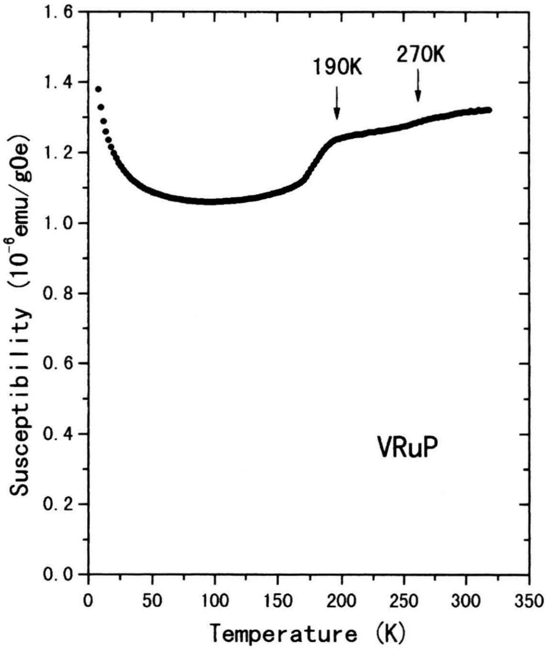

Fig. 3. Temperature dependence of the static susceptibility for a powdered sample of VRuP.

er amounts of vanadium and ruthenium powder of 99.9% purity were mixed with red phosphorus of 99.9999% purity and sealed in an evacuated quartz ampoule. The mixture was sintered for one day at 673 K, and three days at 1123 K, followed by quenching in water. The product was ground, mixed and sealed again in an evacuated quartz ampoule, sintered for three days at 1123 K and quenched in water. The last process was repeated four times to get a homogeneous sample. The crystal structure of the sample was examined by with X-ray powder diffraction. It was confirmed that the sample is a single phase of orthorhombic TiNiSi-type structure (space group Pnma). The lattic constants were determined to be $a = 6.098$ Å, $b = 3.704$ Å, and $c = 6.964$ Å, agreeing well with the [5].

The powdered sample was pressed and sintered for a day, cut into a rectangular solid and used for the resistivity measurement. The temperature dependence of the resistivity, measured with a four-terminal method, is shown in Figure 2. It shows the overall metallic character of VRuP, however two small sudden increases of the resistivity with decreasing temperature are observed at around 270 and 200 K. This behavior is similar to that of $NbSe_3$, which has two successive CDW-transitions [6, 7].

The temperature dependence of the static susceptibility of the powdered sample of VRuP has been measured by a commercial SQUID magnetometer (Quantum Design MPMS-5S). The result (Figure 3) shows an overall Pauli-paramagnetic character of VRuP, however a stepwise decrease of the susceptibility with decreasing temperature is observed at around 190 K together with a quite small one at around 270 K. These temperatures of anomaly in the temperature dependence of the static susceptibility agree with the temperatures at which the temperature dependence of the resistivity has anomalies. The amount of the stepwise change in the susceptibility at around 190 K is estimated to be -2.4×10^{-5} emu/mole, which is nearly the same as that in 1T–TaS_2 or 1T-$TaSe_2$ [7]. This behavior also suggests a decrease of the metallic density of states due to opening of small gaps in the band structure of VRuP.

3. NMR of ^{51}V in VRuP

NMR experiments were performed between 4.2 and 300 K with a home-built, phase coherent pulsed NMR spectrometer. Figure 4 (a) shows a field-swept spin echo spectrum of ^{51}V in a powdered sample of VRuP taken at room temperature at an operating frequency of 17 MHz. Slightly broadened quadrupole satellite lines are observed. The temperature dependence of the spectrum in

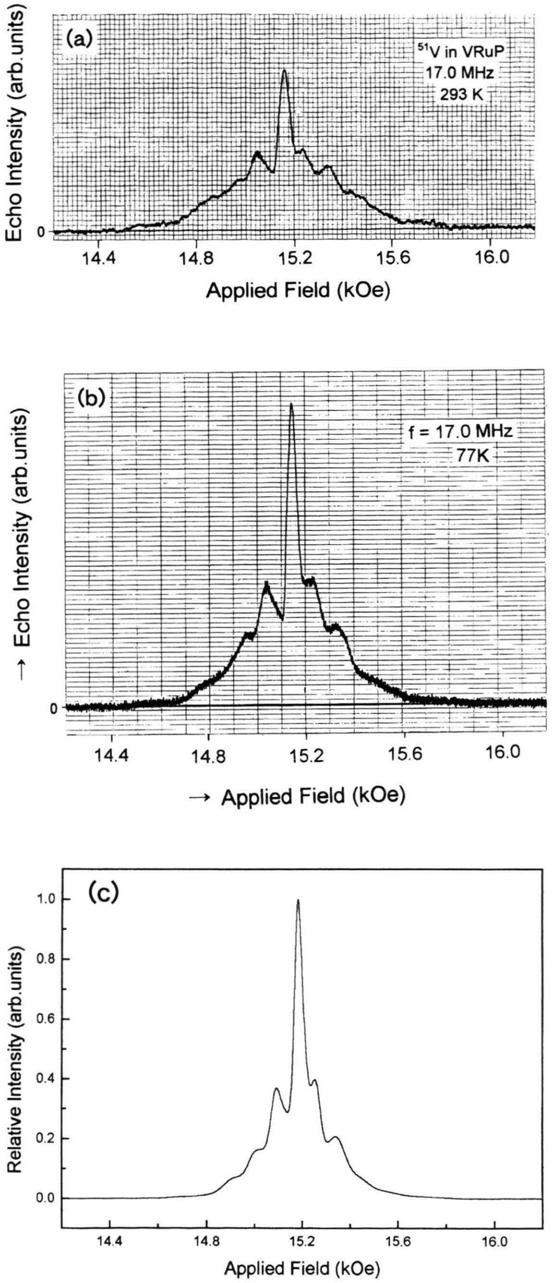

Fig. 4. Boxcar traces of field-swept spin-echo spectra of ^{51}V in VRuP taken at an operating frequency of 17 MHz at room temperature (a), and 77 K (b). A simulated spectrum is also shown (c).

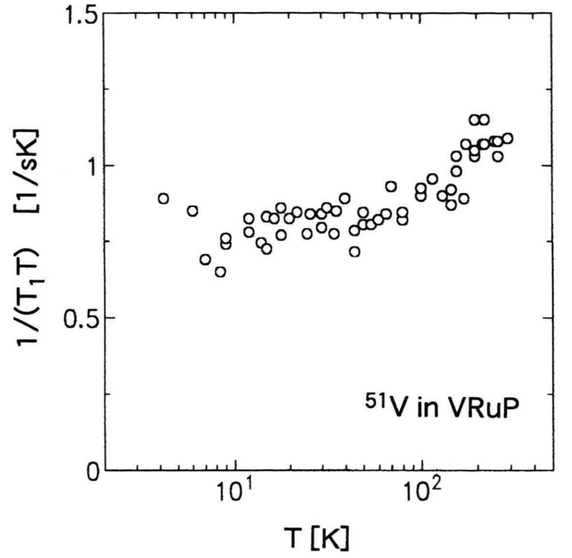

Fig. 5. Temperature dependence of the nuclear spin-lattice relaxation rate of ^{51}V in VRuP, taken at 17 MHz, is shown as $1/(T_1T)$ vs. T.

Figure 4(a) was carefully examined, but no appreciable change of the spectrum was observed around the temperatures of the conductivity anomalies, as Figure 4 (b) shows for 77 K. This suggests that the local symmetry around the vanadium atoms does not change for the majority of the vanadium sites. Simulation of the spectrum was done by assuming Gaussian distributions in quadrupole frequency ν_Q and Knight shift K. The experimental spectrum can be reasonably explained with the following parameters: $\nu_Q = 3e^2qQ/2I\,(2I-1)\,h = 0.21$ [MHz], standard deviation of the distribution in ν_Q of $0.12\nu_Q$, axial part of the shift $K_{ax} = 0.2\%$ and standard deviation of the distribution in the shift of 0.08%, as is demonstrated in Figure 4 (c). The temperature dependence of the nuclear spin-lattice relaxation rate of ^{51}V was measured, and the result is shown in Fig. 5 as a graph of $1/(T_1T)$ versus T. The errors are large because of non single-exponential recovery of the nuclear magnetization. However, it is observed that the metallic rate decreases in a stepwise fashion at around 200 K, suggesting an opening of a partial gap in the band structure of VRuP at that temperature due to, for example, an onset of a charge-density wave transition in this material. The change in the relaxation rate is estimated to be -0.25 s^{-1} K^{-1}, which is about 1/6 of the change in the case of ^{51}V in 1T$-$VSe$_2$ [8]. Further study, using the diffraction method especially for a single crystal is surely necessary to clarify the nature of the transitions.

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