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NMR properties of CoRhP: mixing between Co and Rh sites

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Abstract

NMR properties of ^{59}Co and ^{31}P in CoRhP with orthorhombic TiNiSi structure are reported. Field-swept NMR spectra of ^{59}Co show very broad ones from nonmagnetic Co sites where satellite peaks due to quadrupole interaction are smeared out. The Fourier transformed spectrum of ^{31}P NMR has two peaks. It is suggested that the Co and Rh atoms do not order but their sites are mixed. The mixing is consistent with a Rietvelt analysis of X-ray diffraction powder patterns where a mixing of 10% of Co atoms into Rh sites is estimated. This kind of mixing seems to be one of the origins of the variety of magnetic and electric properties of MRuP and MRhP (M=3d transition metal) systems. The nuclear spin-lattice relaxation rates of ^{59}Co and ^{31}P in CoRhP obey Korringa relations at high temperatures and they show stepwise decreases with decreasing temperature at 11 K where the static susceptibility has a peak. The behaviors are interpreted as an onset of a charge density wave (CDW) at 11 K rather than an onset of an antiferromagnetism. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: NMR; ^{59}Co; ^{31}P; CoRhP; CDW

1. Introduction

Series of ternary compounds MRuP and MRhP (M=3d transition metals) have structures of either the hexagonal Fe_2P or orthorhombic TiNiSi. They show interesting magnetic and conducting properties and present new systems for studying electron–electron correlation in itinerant electron system [1]. A compound FeRuP is an itinerant ferromagnet with a Curie temperature of 184 K [2] and MnRuP is an insulating antiferromagnet at low temperatures [3]. A compound VRuP has been suggested to have charge–density–wave (CDW) transitions at low temperatures [4]. Another compound CrRuP was expected to be in a nonmagnetic state at low temperature such as a Kondo insulator from the susceptibility data and a nonmagnetic NMR signal from ^{31}P. However, zero-field NMR spectra show that it is an antiferromagnet at low temperature [5]. A new compound CoRhP is a member of MRhP that has an orthorhombic TiNiSi structure as shown in Fig. 1. Each cobalt atom is situated in the pyramid formed by five phosphorus atoms. The pyramids are connected by edge sharing to form two-dimensional zigzag network along the *a*–*b* plane. 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 cobalt atoms via apex phosphorus is strong. The temperature dependence of the static susceptibility of CoRhP is shown in Fig. 2 which shows a peak at 11 K. Although the shape of the figure suggests that the compound is an antiferromagnet with a Neel temperature of 11 K, the magnitude of the susceptibility is very small. The feature also contradicts with a former report that it is a simple Pauli paramagnet [6]. The purpose of the present study is to see the electronic state in CoRhP at low temperature from a microscopic viewpoint by doing NMR experiments of ^{59}Co and ^{31}P.

2. Experimental results and discussion

The powdered sample of CoRhP has been synthesized at Tohoku Gakuin University in the following way. Proper amount of cobalt and rhodium powder of 99.9% purity has

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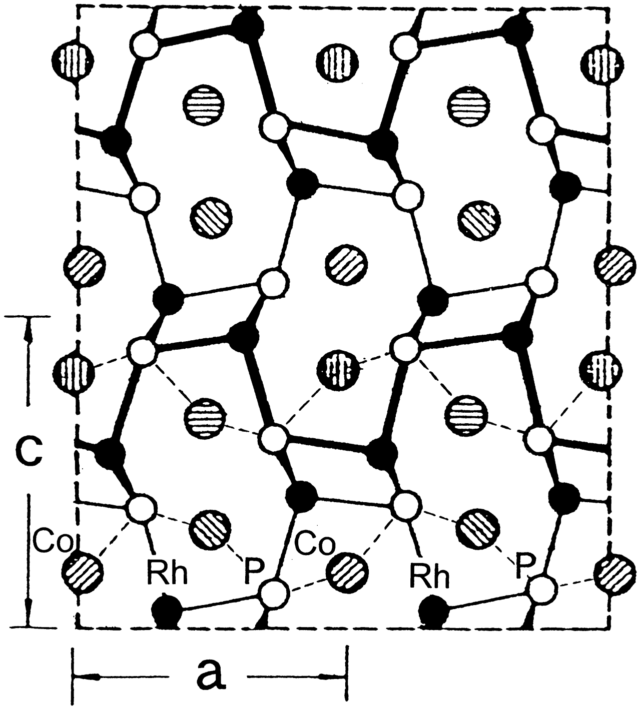

Fig. 1. The crystal structure of CoRhP, where the projection of atom positions on the a–c plane is shown. Atoms connected with thick and thin lines are separated by $b/2$ along the b-direction.

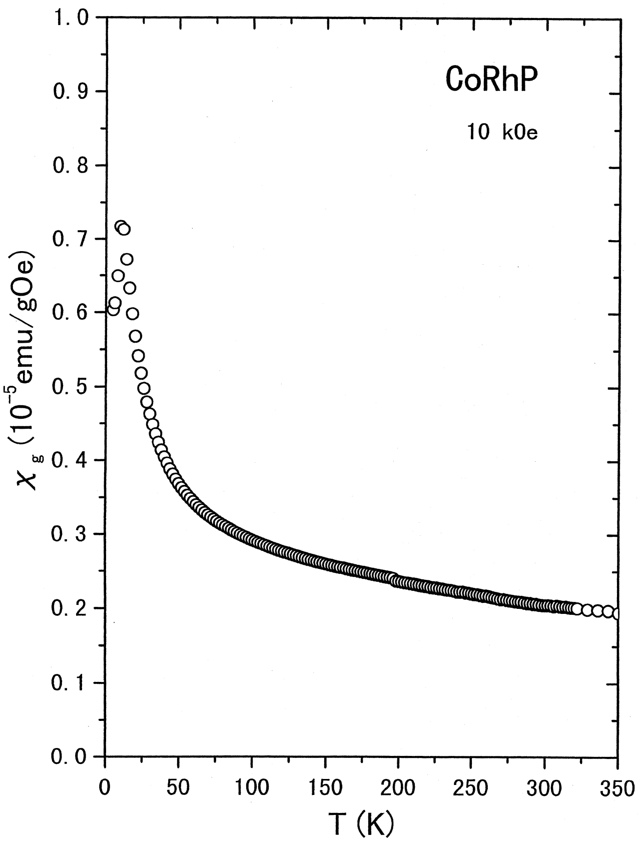

Fig. 2. Temperature dependence of the static susceptibility of CoRhP.

been mixed with red phosphorus of 99.9999% purity and sealed in an evacuated quartz ampoule. It has been sintered for 1 day at 673 K, and 3 days at 1123 K followed by quenching to water. The reactant has been ground and mixed sufficiently and sealed again in a evacuated quartz ampoule, and sintered 3 days at 1123 K followed by quenching to water. The last process has been repeated three times in total to get homogeneous sample. The crystal structure of the sample was examined with X-ray powder diffractometer and it has been confirmed that the sample is in a single phase with an orthorhombic TiNiSi-type structure (space group *Pnma*). The lattice constants has been determined to be $a = 5.791$, $b = 3.640$, and $c = 6.801$ Å which agree well with a previous report [7].

NMR experiments have been performed with a home-built, phase coherent pulsed NMR spectrometers. Field-swept spin echo spectra in powdered sample of CoRhP taken at 77 K are shown in Fig. 3 at operating frequency of 9.0 MHz. Data at 4.2 K are similar. The signal at 5.2 kOe is due to ^{31}P and one at 8.95 kOe is due to ^{59}Co. The signal of ^{59}Co is clearly from nonmagnetic site of cobalt atoms. The spectrum is very broad and satellite peaks due to quadrupole interaction are smeared out. Comparing the spectrum with a well-resolved spectrum of ^{59}Co in Co_3S_4 [8], and with a similar broad spectrum of ^{93}Nb in random environments in Nb–N–B system [9], we conclude that the field gradient at cobalt site has large distribution. A standard deviation of the distribution in the field gradient at cobalt sites is estimated to be about 30% of the magnitude of the field gradient itself by assuming a Gaussian distribution. The line width of ^{31}P is sharp and a Fourier transformed spectra from free decay signal at 300 and 4.2 K are shown in Fig. 4, where two peaks are observed with shifts of 0.00 and −0.05%. The width at 4.2

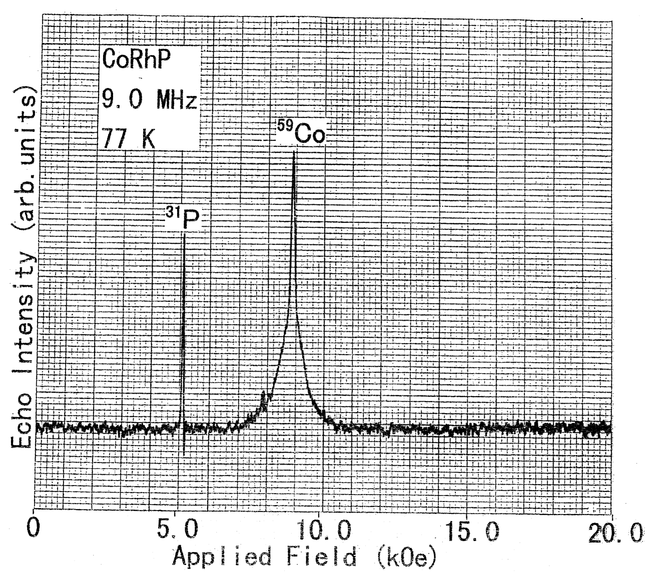

Fig. 3. Field-swept spin echo spectra of ^{59}Co in powdered sample of CoRhP taken at 77 K and an operating frequency of 9.0 MHz.

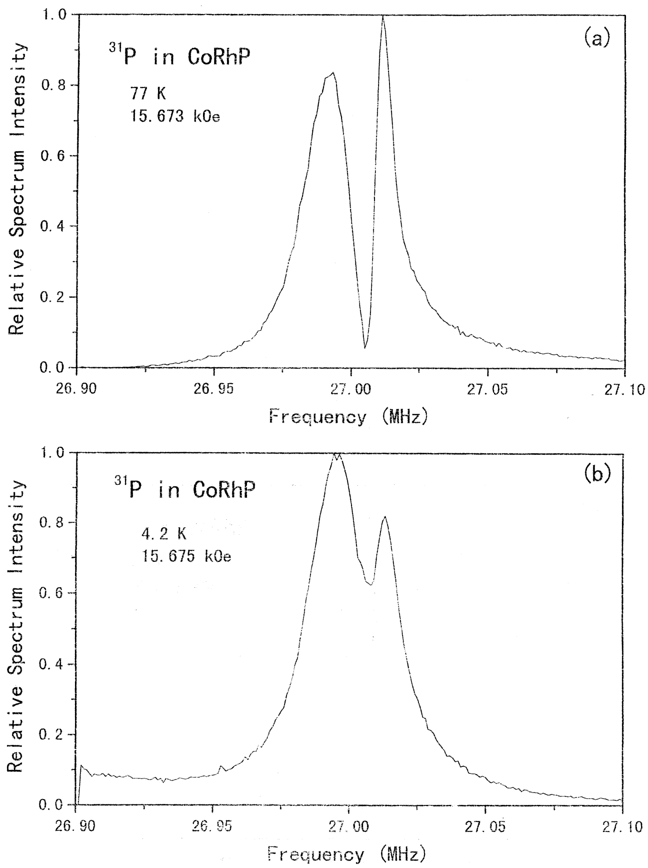

Fig. 4. Fourier-transformed NMR spectrum of ^{31}P in CoRhP in a static field of 15.675 kOe at temperatures of 300 K (a) and 4.2 K (b).

K is larger than that at 300 K, but no appreciable indication of magnetic order is observed. The existence of the two peaks means the existence of at least two sites of phosphorus. From the present NMR data we conclude that the Co and Rh atoms in CoRhP do not order but their sites are mixed. Considering the fact that Co and Rh belong to the same group in the periodic table of the elements and the atomic characters are similar, it does not seem to be unreasonable although the atomic radii are somewhat different. The mixing is consistent with a preliminary Rietvelt analysis of X-ray diffraction powder patterns where a mixing of 10% of Co atoms into Rh sites is estimated. This kind of mixture seems to be one of the origins of the variety of magnetic and electric properties of MRuP and MRhP (M=3d transition metal) since the randomness of the magnetic sites becomes a new degree of freedom. Judging from the NMR spectrum of ^{51}V in VRuP, where the quadrupole satellites are observed, the disorder is less in the case of VRuP [4]. The coexistence of magnetic and nonmagnetic signals in CrRuP [5] is now understood by assuming this kind of atomic disorder. The sample in a former report [6] which has no susceptibility peak might be in a different degree of disorder in Co and Rh sites.

Since no appreciable anomalies has been observed in the temperature dependence of the line shapes of ^{59}Co and ^{31}P in CoRhP, we measured temperature dependence of the nuclear relaxation time T_1 for ^{59}Co and ^{31}P in CoRhP. Typical behavior of the recovery of the nuclear magnetization after saturating rf-comb pulses is shown for ^{59}Co and ^{31}P in Fig. 5a and b, respectively. The recovery of the free decay signal after saturation for ^{31}P is described with a single time constant T_1 over two decades. The relaxation rate T_1^{-1} is considered to be an average rate for the two signals in Fig. 4. The spin-echo signal of ^{59}Co is difficult to saturate because of large width due to quadrupole interaction. The signal after saturation recovers with a very short time constant at first which is probably due to spin diffusion in the spectral space and with a longer temperature-dependent time constant which we interpreted as an intrinsic spin-lattice relaxation time T_1. The obtained temperature dependence of the relaxation rate T_1^{-1} for ^{59}Co and ^{31}P is shown in Fig. 6a and b, respectively. The

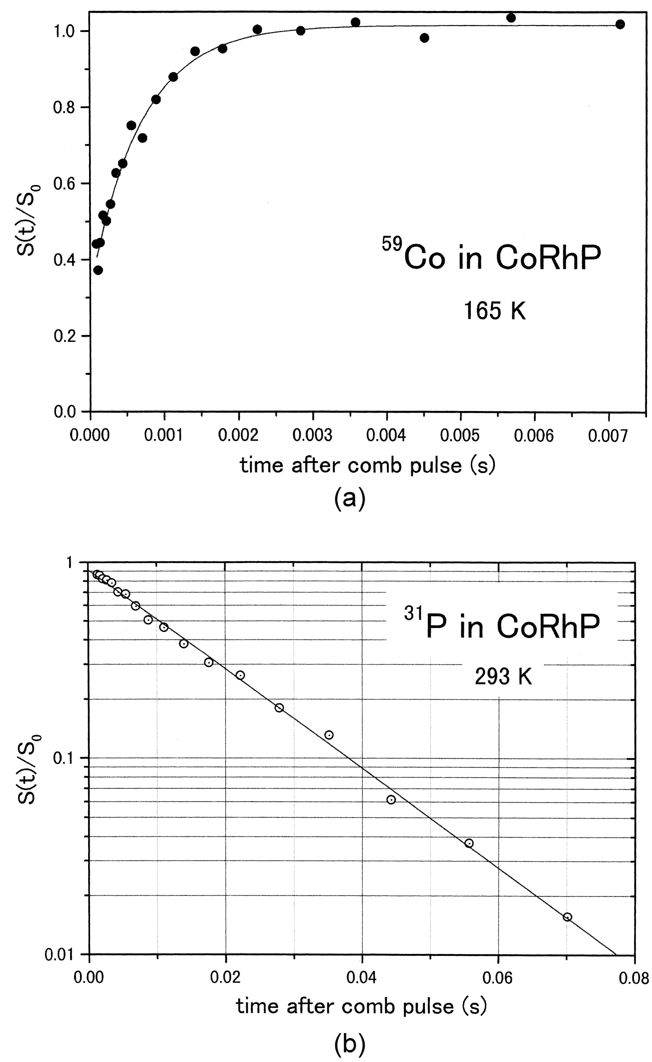

Fig. 5. (a) A recovery of spin-echo signal of ^{59}Co after saturating rf-comb pulses in CoRhP. (b) A recovery of free decay signal of ^{31}P after saturating rf-comb pulses in CoRhP in a logarithmic scale.

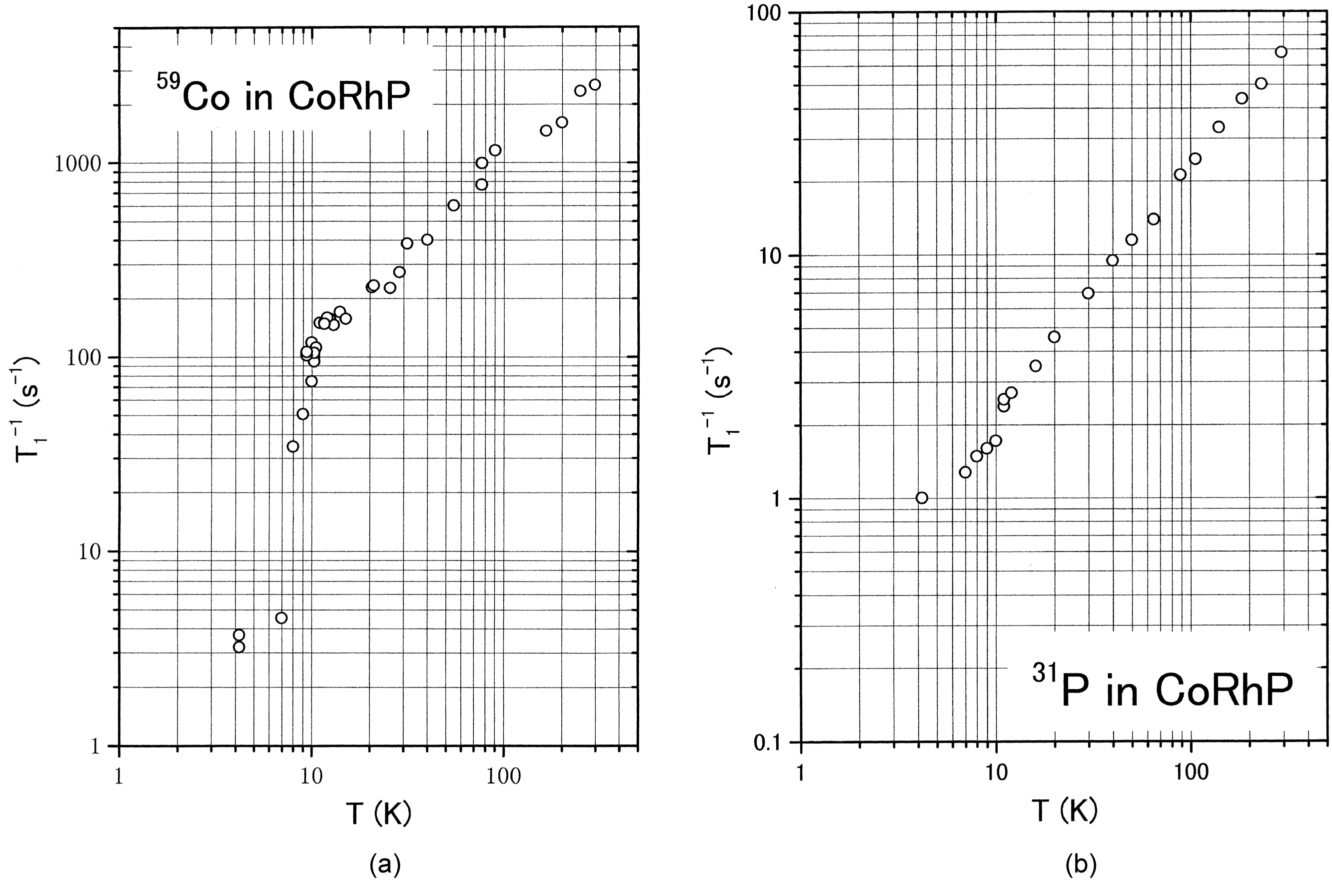

Fig. 6. Temperature dependence of the nuclear spin-lattice relaxation rate T_1^{-1} for ^{59}Co (a) and ^{31}P (b) (see text).

nuclear spin-lattice relaxation rates of ^{59}Co and ^{31}P in CoRhP obey Korringa relations at high temperatures with $(T_1T)^{-1} = 10$ and 0.04 (s^{-1} K^{-1}), respectively, showing the material is not strongly correlated system. Both show stepwise decreases with decreasing temperature at 11 K where the static susceptibility has a peak. No appreciable indication of critical slowing down due to a magnetic ordering is observed. Considering the very small magnitude of the static susceptibility also, the behaviors could be an indication of an onset of a charge density wave (CDW) at 11 K rather than an onset of an antiferromagnetism. The change in the relaxation rate is estimated to be -9.3 (s^{-1} K^{-1}) for ^{59}Co which is 37 times of the change in the case of VRuP [4]. The change in the susceptibility after subtracting a small Curie part at low temperatures is estimated to be -7.0×10^{-4} emu mol^{-1} Oe^{-1} which is abut 30 times of the change in the case of VRuP [4]. Further study using diffraction method especially for a single crystal seems to be necessary to clarify the nature of the transitions.

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