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# NMR spectrum analysis for CrAs at ambient pressure

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## Abstract

We report NMR spectrum analysis for CrAs, which was recently reported to be superconducting under pressure. The NMR spectrum obtained by the powdered single crystals shows a typical powder pattern reproduced by the electric field gradient (EFG) parameters and isotropic Knight shift, indicating anisotropy of Knight shift is not remarkable in CrAs. For the oriented sample, the spectrum can be understood by considering that the crystals are aligned for $H \parallel b$. The temperature dependence of Knight shift was successfully obtained from NMR spectrum with large nuclear quadrupole interaction.

*Keywords:* CrAs, NMR, Knight shift

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## 1. Introduction

A helimagnet CrAs undergoes superconductivity under pressure accompanied by a suppression of the magnetically ordered phase.[1, 2] The helimagnetic transition of $T_N \sim 265$ K at ambient pressure is of strong first order with a large magnetostriction.[3, 4] Because of the large difference in the volume between the paramagnetic (PM) and helimagnetic phases, the ordered phase is easily suppressed by applying pressure of $\sim 0.7$ GPa, and superconductivity occurs with the maximum value of $T_c = 2.2$ K.[1, 2] Although a strong first-order feature of the magnetic transition remains even under pressure, the development of magnetic fluctuations is clearly observed in the nuclear spin-lattice relaxation rate, $1/T_1$.[5] The non-Fermi liquid like behavior in resistivity also suggests that superconductivity of CrAs is realized under strong electronic correlation.[1, 2] To elucidate a relationship between the observed magnetic correlations and superconductivity, Knight shift measurement, which is proportional to the spin susceptibility, gives an important information. That measurement is also important to discuss the parity of the superconducting pairing, that is, whether the superconductivity in CrAs is spin-singlet or spin-triplet. However, such measurements have to be performed carefully, because the estimated nuclear quadrupole interaction at the As site is significantly large compared with prospective Zeeman interaction for NMR measurements. In this paper, we show the NMR results in the PM state at ambient pressure, and Knight shift can be estimated successfully with separating the quadrupole interactions from a careful analysis.

## 2. Experimental procedure

Single crystals of CrAs were prepared by the Sn-flux method from a mixture of Cr:As:Sn=1:1:10 as described in Ref. [2], and they are powdered for NMR measurements to increase the NMR intensity. NMR measurements were performed using the conventional spin-echo method for the $^{75}$As nucleus with the nuclear spin of $I = 3/2$.

## 3. Experimental results and discussion

Figure 1 shows NMR spectrum in the PM state for powdered single crystals, which are fixed in paraffin to avoid an orientation under the magnetic field. The spectrum shows a typical powder pattern, which is reproduced well by a simulation using electric field gradient (EFG) parameters of $\nu_Q = 27.8$ MHz and $\eta = 0.86$, as shown by the red curve. Here, $\nu_Q \equiv 3e^2qQ/2hI(2I-1)$, and $\eta \equiv |V_{xx} - V_{yy}|/V_{zz}$, where $eq \equiv V_{zz}$ is an EFG along the maximum principal axis, and EFG is a 2nd derivative of the electric potential at the nuclear site ($|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$). In the simulation, we take account of only isotropic Knight shift, $K = -1.6$ % to reproduce the spectrum, indicating that anisotropy of Knight shift is not remarkable in CrAs. In the previous NQR

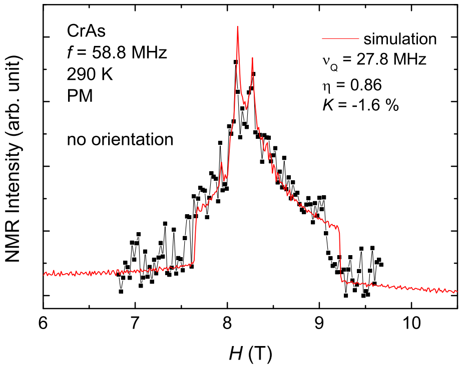

Figure 1: NMR spectrum for the powdered single crystals in the PM state at ambient pressure. The samples are fixed in paraffin to avoid the orientation.

study under pressure,[5] we observed NQR signal in the PM state at $\nu_{res} = 33$ MHz at low temperatures for the $\pm 1/2 \leftrightarrow \pm 3/2$ transition, but $\nu_Q$ and $\eta$ could not be estimated separately, because the observed transition is only one for the NQR. It should be noted that $\nu_Q = 27.8$ MHz and $\eta = 0.86$ obtained from the NMR spectrum at ambient pressure and at 290 K give $\nu_{res} = 31$ MHz, which is comparable to the NQR observation. The EFG at the As site was calculated through an full-potential LAPW (linear augmented plane wave) calculation within the LDA (local density approximation), using the structural parameter reported elsewhere.[6] It gives $\nu_Q = 23.7$ MHz and $\eta = 0.73$, which are almost consistent with the experiment.

Figure 2 shows the direction of the principal axes of the EFG, which are given by the calculation. The maximum principal axis $V_{zz}$ lies in the $ac$ plane, and is tilted by 54.5 ° from the $a$ axis to the $c$ axis. The directions of $V_{zz}$ at the As sites are tilted mutually reflecting the zigzag structure, but all the As sites are equivalent at zero field. If the magnetic field is applied correctly along each crystal axis, the As sites keep the equivalency. The minimum principal axis $V_{xx}$ is calculated to be just along the $b$ axis. It is protected symmetrically that one of the principal axes is along the $b$ axis, because the local symmetry at the As site is $[.m.]$.

Figure 3 shows NMR spectrum for the oriented sample, measured above

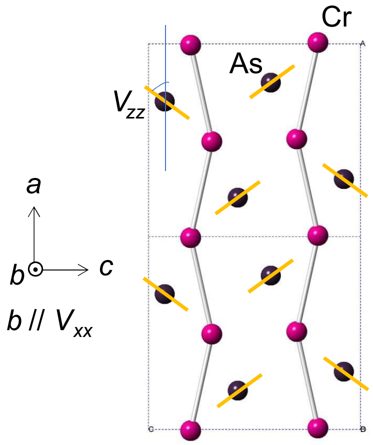

Figure 2: The crystal structure of CrAs and the directions of $V_{zz}$ and $V_{xx}$ at the As site. The yellow bars indicate the direction of $V_{zz}$. The angle between the $a$ axis and $V_{zz}$, shown by blue lines, is estimated to be 54.5$^{\mathrm{o}}$ from the calculation, but it does not affect the present experiment for $H \parallel b$.

$T_N$ at ambient pressure. The orientation was promoted by giving a mechanical shock to the powdered single crystals. The spectrum shape composed of sharp three peaks is quite different from the spectrum for the unoriented sample, ensuring the high degree of the orientation. To reproduce the NMR spectrum, we need five parameters; $\nu_Q$, $\eta$, Knight shift, and the angels between the EFG and the magnetic field in the polar coordinates ($\theta$ and $\phi$). Here, we define that the direction of $V_{zz}$ corresponds to $\theta = 0^{\mathrm{o}}$ and $\phi = 0^{\mathrm{o}}$ Magnetic susceptibility measurements indicate that magnetic anisotropy of CrAs is not large but the $b$ axis is the easy axis at ambient pressure,[7, 8] suggesting that the orientation is achieved for $H \parallel b$. The calculation suggests that $V_{xx}$ is along the $b$ axis, that is, the magnetic field is expected to be along just $V_{xx}$. In this case, $\theta$ and $\phi$ can be fixed to be $\theta = 90^{\mathrm{o}}$ and $\phi = 90^{\mathrm{o}}$. As shown by the red curves, in fact, the observed spectrum is reproduced excellently by a simulation assuming that $H \parallel V_{xx}$. The positions of three peaks show respective temperature dependence, and they make it possible to estimate $\nu_Q$, $\eta$, and Knight shift separately at each temperature.

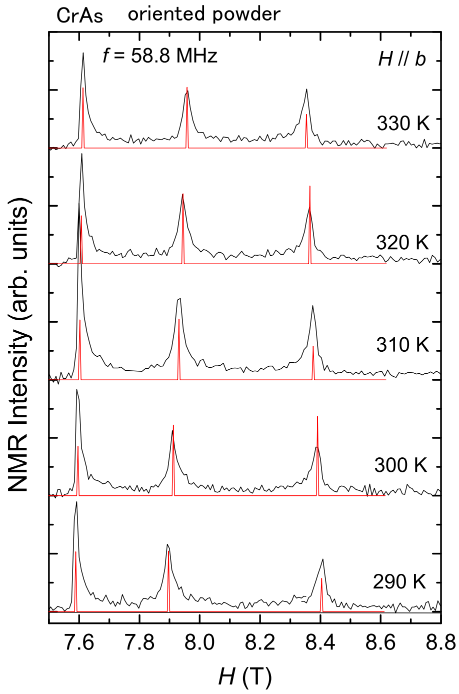

Figure 3: The NMR spectrum for the oriented sample in the PM state. The powdered crystals are considered to be directed for $H \parallel b$. The peak positions are shifted against temperature because of the temperature variation of $\nu_Q$, $\eta$, and Knight shift. The red curves indicate the simulations for $H \parallel V_{xx}$.

The temperature dependences of $\nu_Q$, $\eta$, and Knight shift are shown in Fig. 4. The obtained $\nu_Q$, $\eta$, and Knight shift at 290 K are excellently consistent with those obtained for the unorientaed sample, described in Fig. 1. The $\nu_Q$ and $\eta$ has temperature dependence probably because of the thermal expansion of the lattice. On the other hand, Knight shift has negative sign and its absolute value decreases with decreasing temperature. From the temperature dependence of the magnetic susceptibility,[7, 8] which shows a decrease with decreasing temperature, the hyperfine coupling constant in the spin part, $A_s$ is found to be negative from the relation of $K(T) = A_s\chi_s(T) + K_{orb}$. It is difficult to estimate he values of $A_s$ precisely owing to the insufficiency of the temperature range for the fitting, but the rough estimation gives approximately $A_s \sim -12$

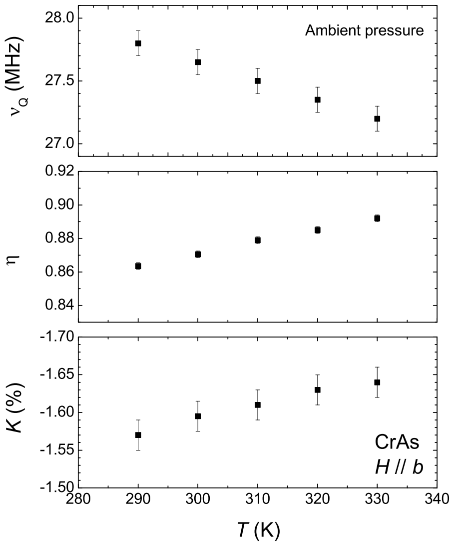

Figure 4: The temperature dependences of $\nu_Q$, $\eta$, and Knight shift at ambient pressure.

kOe/$\mu_B$ for $H \parallel b$ using the susceptibility data for the single crystal.[7] The negative hyperfine coupling is attributed to the core-polarization effect through the hybridization of As $p$ orbit and Cr $d$ orbit.

## 4. Summary

We performed $^{75}$As-NMR measurements for the unoriented and oriented samples of CrAs. The careful analysis with combining the calculation of the EFG makes it possible to estimate the Knight shift from the NMR spectrum affected by the nuclear quadrupole interaction. At present, we are performing NMR measurement under pressure, especially using a single crystal, to discuss the magnetic properties near the superconducting phase and the magnetic anisotropy of CrAs, which will be reported elsewhere.

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