⁵⁹Co-NMR Knight Shift of Superconducting Na_xCoO₂·yH₂O

Yoshiaki Kobayashi, Mai Yokoi and Masatoshi Sato

Department of Physics, Division of Material Science, Nagoya University, Furo-cho, Chikusa-ku

Nagoya, 464-8602 Japan

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Layered Co oxide $Na_xCoO_2\cdot yH_2O$ with the superconducting transition temperature T_c =4.5 K has been studied by ⁵⁹Co-NMR. The Knight shift K estimated from the observed spectra for powder sample exhibits almost temperature(T)-independent behavior above T_c and decreases with decreasing T below T_c . This result and the existence of the coherence peak in the spin-lattice-relaxation-rate *versus* T curve reported by the present authors indicate, naively speaking, that the singlet order parameter with s-wave symmetry is realized in $Na_xCoO_2\cdot yH_2O$. Differences of the observed behaviors between the spectra of the non-aligned sample and the one aligned in epoxy adhesive by applying the external

corresponding author: M. Sato (e-mail: e43247@nucc.cc.nagoya-u.ac.jp)

magnetic field are discussed.

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The recent discovery of superconductivity in the layered cobalt oxide $Na_xCoO_2\cdot yH_2O^{-1}$ has attracted much attention, because it has the triangular lattice of Co atoms. The system can be obtained from Na_xCoO_2 by deintercalating Na^+ ions and simultaneous intercalating H_2O molecules. The superconducting transition temperature T_c was reported to be ~5 K. Up to now, various kinds of experimental and theoretical studies have been carried out to investigate the mechanism of the superconductivity¹⁻¹⁶.

In the previous report, the present authors have shown by 59 Co-NQR studies of the system, that the coherence peak of the 59 Co-nuclear spin relaxation rate $1/T_1$ exists just below T_c . It has been also pointed out, based on detailed comparison of the relaxation rates $1/T_1$ and the magnetic susceptibilities χ between Na_xCoO₂·yH₂O and Na_xCoO₂ that the former system is closer to the ferromagnetic phase than the latter⁷).

In the present paper, the temperature (T) dependence of Knight shift K studied by ⁵⁹Co-NMR of Na_XCoO₂·yH₂O is reported. Then, based on the observed behaviors of K and $1/T_1$, the paring symmetry is argued.

The powder sample of Na_xCoO₂·yH₂O with $T_c \sim 4.5$ K was prepared from Na_{0.75}CoO₂ by the method described in Ref. 1. The structural and magnetic properties of the sample were reported in the previous paper⁷). The NMR experiments were carried out using a standard phase coherent type pulse spectrometer. ⁵⁹Co NMR spectra were obtained by recording the spin-echo intensity with the applied magnetic field changed step by step in a magnetic field range of 1-2 T. Measurements were carried out on two kinds of samples of Na_xCoO₂·yH₂O, randomly oriented and aligned samples. The latter sample was prepared by mixing the Na_xCoO₂·yH₂O powder with epoxy adhesive (Stycast 1266) and keeping the mixture in a magnetic field of 11T at room temperature for ~12 h Its X ray diffraction pattern indicates that the *ab* plane of Na_xCoO₂·yH₂O crystallites align along the direction of the magnetic field with the spreading of about (±6°). (The lattice parameter *c* was found not to exhibit significant change after the alignment processes, which indicates no drastic change of the structure.) The former sample does not have epoxy adhesive. It was just put into a cylindrical holder made by cellophane tapes. The obtained spectra are shown in Fig. 1(a) and 1(b) for randomly oriented powder and aligned samples, respectively.

The positions of the peaks and shoulders of the 59 Co-NMR spectra observed for both kinds of samples were well explained by considering the anisotropic Knight shifts $K_x \neq K_y \neq K_z \neq K_x$ and the effects of electric quadrupole interaction up to the second order. The directions of the principal axes of Knight shift are assumed to be same as those of the electric quadrupole interaction. In the present case, the z-axis was defined along the direction, for which the component of the electric quadrupole tensor, v_{zz} is larger than the other components. This z direction was found to be along the c-axis by fitting the positions of calculated spectra to those of aligned sample. The fitted result for the data taken at 5 K in the magnetic field H within the ab plane of $Na_xCoO_2 \cdot yH_2O$ is shown in Fig. 1(b) and the parameters

determined by the fitting are, $K_x = \sim 3.5 \pm 0.1$ %, $K_y = \sim 3.1 \pm 0.05$ %, the electric quadrupole resonance frequency $v_Q = 3.6 \pm 0.05$ MHz and the asymmetric parameter of the electric field gradient at nuclei $\eta = 0.28 \pm 0.02$. For the spectra of the randomly oriented sample, $K_x = \sim 3.8 \pm 0.1$ %, $K_y = \sim 3.14 \pm 0.05$ %, $K_z = \sim 2.3 \pm 0.2$ %, $v_Q = 4.05 \pm 0.05$ MHz and $\eta = 0.24 \pm 0.01$ were found to reproduce them well. The comparison of the values of v_Q and η of the aligned sample with those of the randomly oriented one justifies the present assignment of the z direction along the c axis.

Figure 2 shows the T dependence of the ⁵⁹Co-NMR spectra around the peak of central line for the randomly oriented powder sample. The H value of the peak position is nearly T-independent above T_c (~4.5 K) and then increases with decreasing T below T_c . This change of the peak position is due to the T dependence of the Knight shift K_y and not due to the second order effect of the electrical quadrupole interaction, because v_Q and η are T-independent, as was confirmed by analyzing the spectra in the H region between 0.8-2.4 T at 2.9 K, 4.7 K and 6.2 K.

It should be noted here following facts. For the aligned sample, the peak position of the central line of the 59 Co-NMR spectra, which corresponds to K_y , is nearly T-independent even below T_c . It is slightly puzzling, because the result indicates that the T dependence of K_y of the aligned sample is different from that of the powder sample. To explain this puzzle, we consider that the shift K_y observed in ref. 8 for a sample aligned in epoxy adhesive (Stycast) also exhibits the T-independent behavior. We think that the specimens embedded in the Stycast have somewhat different properties from those of the (non-aligned) samples. This idea is supported by the fact that we have observed different values of K_x between the two kinds of samples, which has already been stated above. Then, the data of the aligned sample may not be intrinsic.

We have estimated the K_y value of the (non-aligned) powder sample. The results are shown in Fig. 3. Above T_c , K_y is nearly constant and decreases with decreasing T below T_c . Because we have already taken into account the effect of the electrical quadrupole interaction up to the second order in the estimation of K_y , the decrease of K_y below T_c with decreasing T should be due to the T dependence of its spin component $K_{\rm spin,y}$ and/or due to the effect of the shielding diamagnetism (The orbital component $K_{\rm orb,y}$ may be T-independent.) Here, in order to estimate the change of the magnetic field at the Co nuclei by the shielding supercurrent, we consider the case where the H is applied along the y direction, i.e., within the a-b plane of the crystallites, because we are observing K_y . For the penetration depth λ of 5000~8000 Å at low temperatures, $^{3,6)}$ we expect that the reduction of the field is roughly one order of magnitude smaller that the observed shift of the peak. It has been confirmed by the following experimental observation. Even when the measuring frequency is changed from 16.09 MHz to 30.044 MHz, the Knight shift does not change within the experimental error bars, indicating that the spatial variation of the field or the shielding effect is negligible in the present experimental condition. It is also confirmed by studying experimental observations for the similar two-dimensional system YBa₂Cu₃O₇ with λ (~1400 Å at T<< T_c) larger than that of the present system does not have a serious

effect of the shielding diamagnetism in the vortex state (at H=7.4 T).¹⁷⁾ Furthermore, it can be noted that the shape of the peak corresponding to K_y does not exhibit an appreciable change expected in the case where the spatial variation of H induced by the shielding diamagnetism is a main cause of the shift.

We have just tried to fit the K_y -T curve below T_c by the Yosida function¹⁸⁾ (see the solid curve in Fig. 3) and obtained the superconducting energy gap Δ of 8.1 K. For the value and T_c =4.5 K, $2\Delta/k_BT_c$ is estimated to be 3.6, which agrees well with the one expected from the BCS theory, though the rather good fitting by the Yosida function may be accidental. To estimate $K_{\text{spin},y}$ precisely, we have to know the orbital component $K_{\text{orb},y}$, which is, at this moment, not easy.

Now, we have shown that the spin susceptibility $\chi_{\rm spin}$ of Na_xCoO₂·yH₂O studied by measuring the Knight shift K_y decreases with decreasing T in the superconducting state. The existence of the coherence peak of the nuclear relaxation rate $1/T_1$ just below T_c has also been reported in the previous paper by the present authors.⁷⁾ These results indicate, naively speaking, that the superconducting pairs of Na_xCoO₂·yH₂O are in the singlet spin state with s-wave symmetry, though other possibilities may not be completely ruled out: Strictly speaking, the (d_1+id_2) state predicted in refs. 10-13 may have a small coherence peak. Then, the precise calculation of the amplitude of the coherence peak is required to exclude such the symmetry. Even for the p-wave state predicted in refs. 14 and 15, the decrease of $K_{\rm spin}$, p can be expected, if the direction of the triplet spins is pinned in the direction perpendicular to the p-axis. At this moment, we do not know how strong the pinning force is. To answer this question, further studies on the anisotropy of the Knight shift has to be carried out by using single crystal specimens.

In summary, the T dependence of the Knight shift K_y of Na_xCoO₂·yH₂O has been reported. For the (non-aligned) powder sample, the T dependence of the spin component $K_{\text{spin},y}$ roughly follows the Yosida function in the superconducting state. This behavior and the existence of the coherence peak in the $1/T_1$ -T curve observed just below T_c indicate that Na_xCoO₂·yH₂O has the spin singlet pairs with the s-wave symmetry, though the observed results do not completely exclude the possibility of other kinds of electron pair state.

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Figure captions

- Fig. 1(a) 59 Co-NMR spectra of Na_xCoO₂·yH₂O taken at T = 4.72 K and with the resonance frequency f = 16.09 MHz for the randomly oriented sample. Solid line is just for the guide to the eye.
- Fig. 1 (b) ⁵⁹Co-NMR spectra of Na_xCoO₂·yH₂O taken at T =4.72 K and with the resonance frequency f =16.09 MHz for the aligned sample, where the powder of Na_xCoO₂·yH₂O is embedded in the epoxy adhesive (Stycast 1266). Solid line is just for the guide to the eye. Broken line shows the spectra calculated with the parameters K_x =~3.5 %, K_y =~3.1 %, V_Q =3.6 MHz and η =0.28.
- Fig. 2 Profiles of the sharp peak of the central line taken for the randomly oriented powder sample at several fixed temperatures are shown. The peak positions correspond to the Knight shifts K_y . The vertical broken line shows the peak position above T_c .
- Fig. 3 Knight shift K_y is plotted against T. The solid line shows the Yosida function fitted to the data.

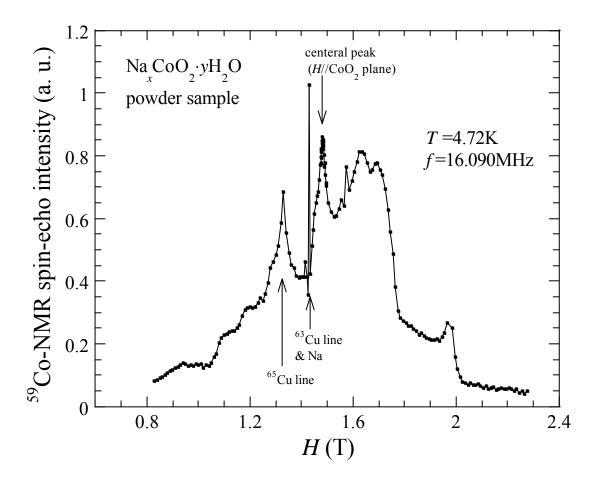


Fig. 1(a)

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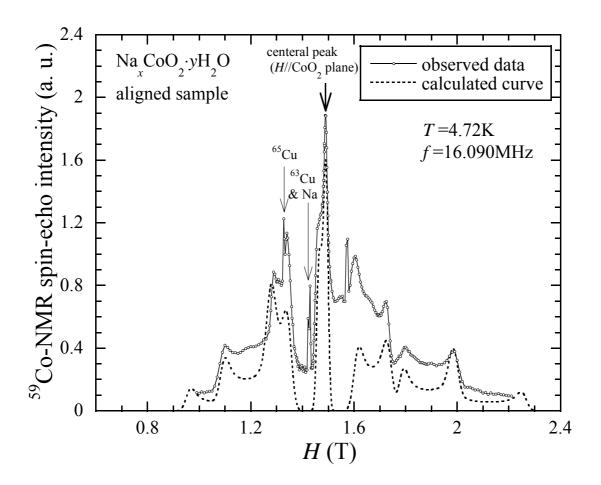


Fig. 1(b)
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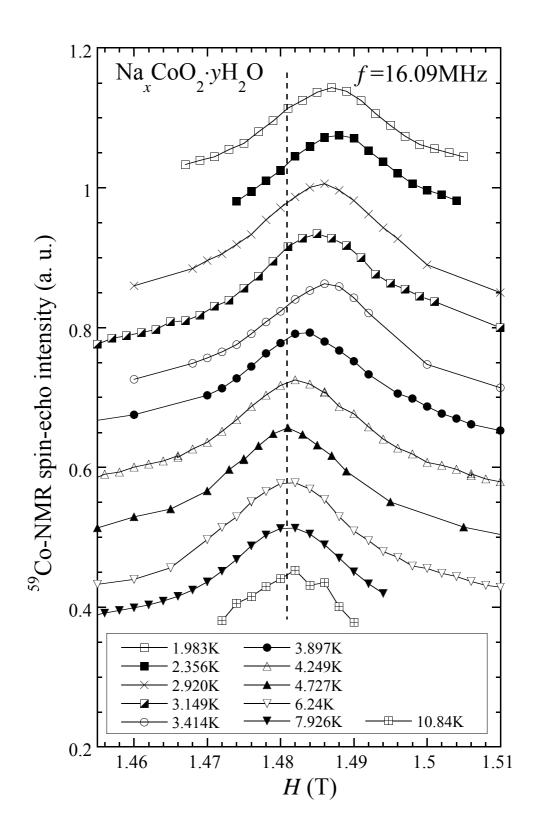


Fig. 2 Y.Kobayashi *et al*.

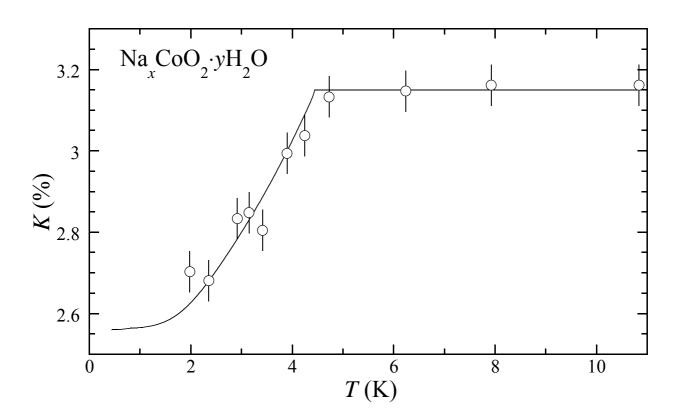


Fig. 3 Y. Kobayashi *et al*.