Distribution of Electric Field Gradient at Aluminum Sites in Zeolite Loaded with Potassium

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In the zeolite LTA, loaded with potassium, the temperature and field dependence of ^{27}Al NQR was observed. Symmetrical single shoulders are found on both sides of the central line. The shape and the shift of those shoulders show no dependence on both temperature and the strength of the external field. This evidences a first order electric quadrupolar shift, being the result of the distribution of the nuclear quadrupole coupling constant and the asymmetry parameter at ^{27}Al sites.

Key words: Zeolite; LTA; Potassium; ^{27}Al NQR; First Order Quadrupolar Shift; Electric Field Gradient; Distribution.

1. Introduction

In the time for the study of magnetic materials by NMR, two kinds of nuclear sites are to be planned for the observation of the signal. One is the on site nucleus to the magnetic electrons and the other is the surrounding site. The former has advantage in the strength of the effect from electron, but, since the effect is sometime so large to give wide line width and huge shift, the signal itself often gives problems for observation. On the other hand for the latter, the effect itself is relatively weak but small shift or precise line shape can be investigated through, for example, the field or the temperature dependence and so on. For the case of zeolite loaded with potassium, which shows ferromagnetism [1], nucleus of potassium corresponds to the former case [2]. Since, unfortunately, the gyromagnetic ratios are fairly smaller than usual nuclei, the investigation by ^{39}K and ^{41}K is not easy to be done. Then the nuclei for latter case, ^{29}Si or ^{27}Al, become important for practical investigations. Although, in a sense of magnetic study, ^{29}Si (nuclear spin $I = 1/2$) is more ideal than ^{27}Al ($I = 5/2$) among these two, ^{27}Al still has some more advantage than ^{29}Si because the signal intensity of ^{27}Al is much larger than ^{29}Si owing to the natural abundance. Then a remaining problem for ^{27}Al is, "how to eliminate the effects of nuclear quadrupole coupling with electric field gradient". In this study, we observed temperature and field dependence of ^{27}Al NMR spectrum of zeolite LTA loaded with potassium and considered the property of nuclear quadrupole coupling.

2. Experimental

Dried zeolite LTA, whose chemical formula is $K_{12}Al_{12}Si_{12}O_{24}$, has an aluminosilicate network [3]. Attracted by the charge compensation ion K, vaporized potassium atoms are adsorbed between the network [2]. An α cage or one kind of periodical spaces is selected by nature among two for the place to be located [2]. The ferromagnetism of the potassium-adsorbed system originates from the periodical configuration of the space [3]. In this study, the transition temperature of the sample is 6 K. 5.2 potassium atoms are contained per one α cage. Sample preparation has been done in the same way as in [4].

The observation of ^{27}Al NMR has been done in a constant field of 11.74 T. The spectrum was recorded by plotting the echo intensity with changing frequency. For the field dependence experiments in lower fields, such as 5.88 T and 1.15 T, the intensity of the spin echo was recorded with a sweeping external

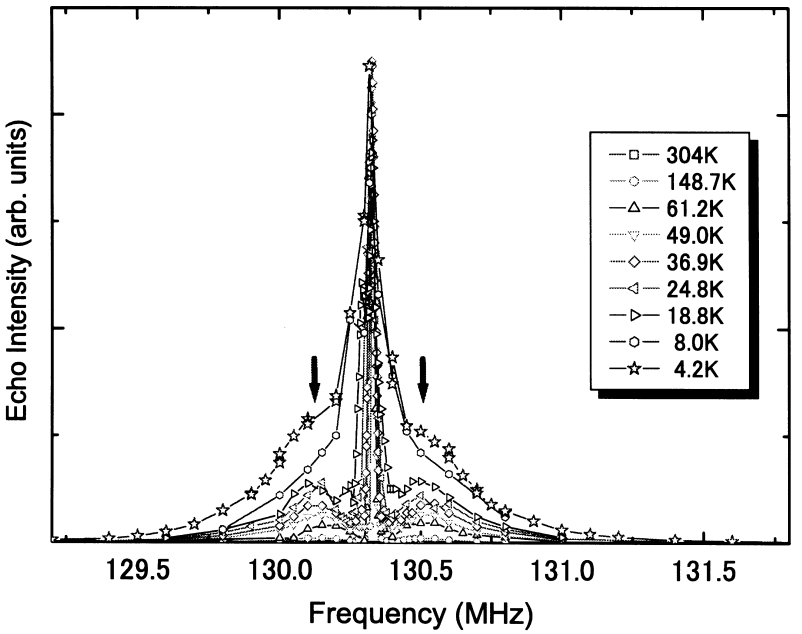

Fig. 1. Temperature dependence of the ^{27}Al NMR spectrum of the zeolite LTA loaded with K. The intensity is normalized to become equal at the central peak. For the low temperatures the relative intensity of side parts becomes larger by the widening of the central part caused by the paramagnetic species.

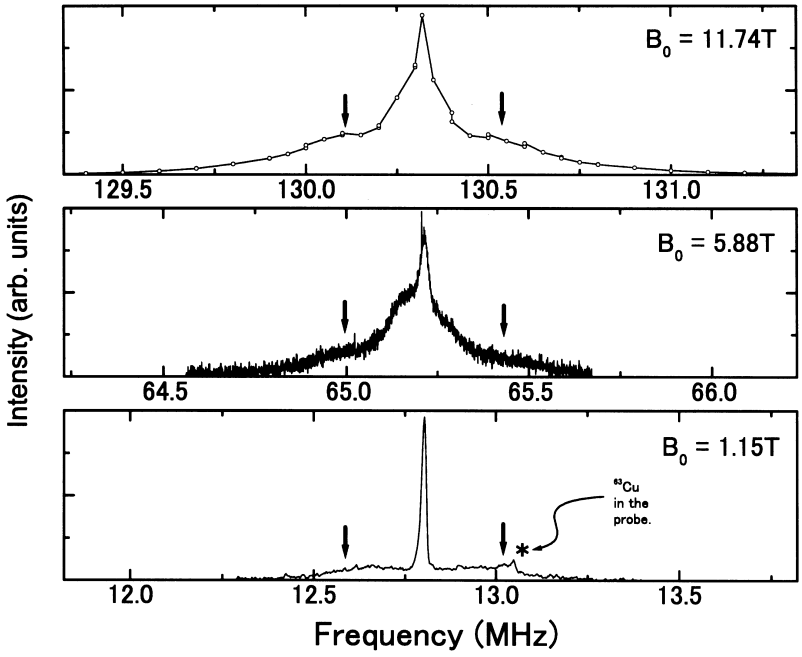

Fig. 2. ^{27}Al NMR spectra of LTA loaded with K at 4.2 K in various fields. The small peaks under the arrows keep constant the absolute shifts on both sides of the central peak. This is a feature of first order satellites.

magnetic field. In the figures, the scale of the field is changed into frequencies using the gyromagnetic ratio.

3. Experimental Results and Discussion

The temperature dependence of the ^{27}Al NMR spectrum is shown in Figure 1. The width of the central area increases with decreasing temperature and is explained above 14 K by the local field from paramagnetic electrons in an α cage. Additional widening occurs below 14 K because of some transitions. These successive changes are similar to those previously reported for ^{29}Si NMR [5].

A main difference from ^{29}Si NMR is the existence of satellites, marked by arrows in the figure, appearing

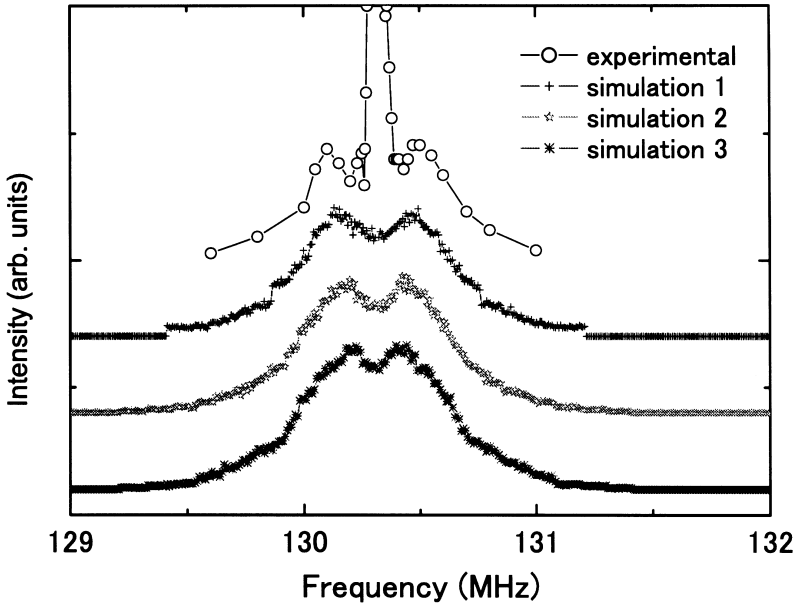

Fig. 3. Simulated curves, using the obtained best fit parameters. The experimental curve of the ^{27}Al NMR spectrum at 4.2 K in 11.74 T is also shown. Simulation 1: ν_Q is fixed at 0.45 MHz and η ranges from 0.2 to 0.6. Simulation 2: ν_Q ranges from 0.33 to 0.55 MHz and $\eta$is fixed at 0.7. Simulation 3: ν_Q ranges from 0.33 to 0.55 MHz and η ranges from 0.6 to 0.4. Several variations of the parameters result in the same tendency.

on both sides of the central line particularly at lower temperatures. Since the shifts of those shoulders are almost temperature independent, the origin of the shift is expected as being caused by the nuclear quadrupole interaction. For this, we consider two explanations: One is a second order quadrupolar shift and the other is a first order satellite. The former has an inverse dependence on the field, and the latter does not depend on the field [6]. We observed the spectra also at lower fields, cf. Figure 2. As pointed by the arrows, the absolute shift of the weak shoulders does not change with the field. Therefore this is a first order satellite shift. And, simultaneously, the possibility of chemical shift is also denied. On the other hand, the width of the central area becomes drastically narrower on decrease of the field. This positive dependence on the field is not due to quadrupolar interaction but corresponds the magnetization growth of paramagnetic electrons in an α cage.

Since the nuclear spin of ^{27}Al is 5/2, two satellites or first and second peaks must be observed on each side when the nuclear quadrupole coupling constant ν_Q and the asymmetry parameter η are identical for all sites (except for the case of $\eta \cong 1$). But, actually, only one shoulder is seen on each side. This fact makes us suppose several sites with different ν_Q and η. This seems to occur in the zeolite. Since the bond length between Al and O is slightly different from that between Si and O [4], one can suppose that the bonding angle around an Al atom is different from site to site. Moreover, an introduction of external atoms may deform the Al-O-Si network. As the separated peaks and "valleys" on the two shoulders of the central line are shallow, the asymmetry parameter η is expected to be much smaller than unity, which results in a merging of center and satellite lines and gives simple slopes on both sides [6]. To get more information, numerical simulation is required. Here we do that to have a bird's eye view for the feature of the parameters ν_Q and η. Following [6], so called powder patterns of first order satellites are calculated with various ν_Q and η.

We here pay our attention only to the shape of the spectrum and set the maximum of ν_Q as 1. One can later fit experimental data to the shape by rescaling the frequency axis. We assumed a homogeneous distribution of ν_Q and η in each range for every condition. Since we don't have knowledge about the distribution, the assumption of special distributions makes the problem more complicated. The trying procedures we have performed to seek for ideal parameters were as follows:

(I) Case of identical ν_Q and distributed η: ν_Q is fixed as unity in this case. The distribution of η from 0.2 to 0.6 was best in this category but was still insufficient. For a narrower range of the η-distribution, the reconstructed shape is quite far from the experimental one. More than one peak remains on both sides. A tuning of η does not eliminate step like features.

(II) Case of distributed ν_Q and $\eta = 0$: Distribution of ν_Q from 0.6 to 1.0 was best in this category. Both wider and narrower ranges of distributions give multiple peaks on each side. Every case contains many sharp edges coming from each ν_Q contribution. Accepting the result of this step, we fixed the variation range of ν_Q from 0.6 to 1 in the following procedures.

(III) Case of distributed ν_Q (0.6 - 1.0) and varied identical η: η in the range from 0.5 to 0.7 gives quite like shape to the experiment.

(IV) Case of distributed ν_Q (0.6 - 1.0) and upward-varied η: In any variation range of η, like shape can not be obtained. Sharp peaks remain on the spectrum or peaks disappear. Not good.

(V) Case of distributed ν_Q (0.6 - 1.0) and downward-varied η: Variation of η from 0.5 to 0.3 was the best one and most like one. For wider variation, unnatural bending point remains at outer side of the peaks. It seems that narrower range variation is better than wider range.

The best-simulated curves using the obtained parameters are shown in Figure 3. By the procedure (II), we see that half range distribution of ν_Q gives good results. If ν_Q distributes as this type, we see by the procedure from (III) to (V) that η is expected to be ranged for not so wide. An middle range value around 0.5 is most preferable. If ν_Q does not distribute and takes identical value for each site, a wide range variation of η is required to show experimental spectrum. We conclude possible distributions of ν_Q and η as follows:

(i) $\nu_Q = 0.45 \pm 0.5$ MHz, $\eta = 0.2 \sim 0.6$,
(ii) $\nu_Q = 0.33 \sim 0.55$ MHz, $\eta = 0.6 \pm 0.1$.

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