JOURNAL OF SOLID STATE CHEMISTRY 32, 119–122 (1980)

Evidence for Proton Pairs in γ-AlOOH (Boehmite) from NMR Absorption Spectra

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Received January 2, 1979; in final form June 19, 1979

Continuous-wave and Fourier transform NMR absorption spectra have been recorded for pure γ-AlOOH at room temperature and 130 K. The well-resolved doublet lineshape shows that there are proton pairs (intrapair separation $R \simeq 1.7$ Å), the presence of which has not previously been recognized. A structural model based on the occupation of two sites consistent with the space group *Cmcm* is proposed.

Introduction

The structure of boehmite (γ-AlOOH), which occurs in nature and can be synthesized in the laboratory, has not been completely determined. The principle feature is known to be layers (of edge- and corner-shared AlO_6 octahedra) which are held together by hydrogen bonds (*1*). Studies by X-ray powder techniques (*2–4*) have suggested the space groups *Cmcm* and *Cmc*2_1, the former being more probable. No single-crystal studies have been published and the hydrogen atoms have not been located.

NMR (*5–8*) and IR (*9, 10*) studies of γ-AlOOH have been interpreted in terms of a zig-zag chain of hydroxyl groups involved in asymmetric hydrogen bonds between the layers. Hydrogen atom diffusion is believed to occur via OH_2^+ defects in the hydroxyl chain (*11, 12*). In the present work, we examine the ^{1}H NMR absorption spectra of γ-AlOOH more closely and find that further information is available from them.

Experimental

γ-Al_2O_3 was reacted with water in an autoclave at 350°C and 175 atm for 5 days. The X-ray powder pattern of the product was consistent with those reported for γ-AlOOH (*2–4*) and corresponds to a pure orthorhombic phase with $a = 2.868(1)$ Å, $b = 12.205(9)$ Å, and $c = 3.693(2)$ Å. Thermal decomposition of the product on a vacuum microbalance gave a weight loss of 14.7%, the theoretical value being 15.0%. The IR absorption spectrum of the product agreed with those previously reported (*10, 11*).

The room-temperature NMR absorption spectrum was recorded using a Bruker continuous-wave (CW) wide-line spectrometer operating at $\omega_0/2\pi = 30$ MHz with a modulation width of 1 G and is shown in Fig. 1. The second moment, M_2, of the absorption line (less the central peak) is, after correction for modulation broadening (*13*),

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0022-4596/80/040119-04\$02.00/0

Printed in Great Britain

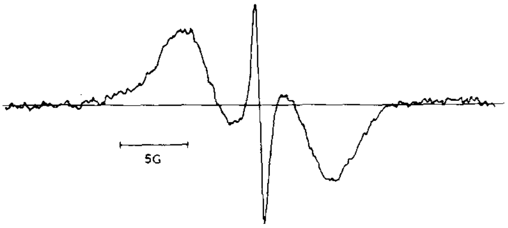

FIG. 1. NMR absorption signal first derivative for γ-AlOOH at room temperature recorded using a modulation width of 1 G.

17.5 G^2. Further absorption spectra were produced by Fourier transformation using a Bruker CXP pulse spectrometer operating at $\omega_0/2\pi = 90$ MHz. Figure 2 shows the room temperature spectrum produced from accumulated free-induction-decays. The central line was not present in spectra at 130 K. However, the broad spectrum was not significantly altered and is that of a rigid lattice. Even though the doublet splitting is unreliable because of uncertainty in the time zero, the central line is negligibly affected. Spectra produced using the zero-time-resolution technique (*14*) do not suffer from this but are distorted by dipolar error terms. M_2 values can, however, be calculated with accuracy from the curvature of solid echoes at their maxima (*15*) and this gave $M_2 = 18.1 \pm 0.5\ G^2$, in agreement with the CW value and those previously reported (5–7).

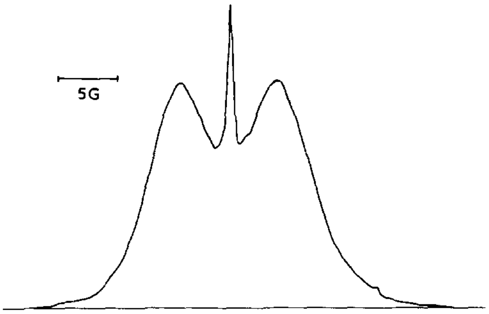

FIG. 2. NMR absorption signal for γ-AlOOH at room temperature produced by Fourier transformation of 400 accumulated free-induction-decays. The central line is <1% of the total absorption signal and is absent at 130 K.

Discussion

The NMR absorption lineshape for γ-AlOOH is a Pake doublet (*16*) with an additional, very narrow, central line at room temperature. The doublet is also evident in the spectra given by Fripiat and Touillaux (*8*), who did not comment on it.

The central line is, as first suggested by Rouquerol *et al.* (*17*), probably due to nonconstitutional water molecules, trapped in the lattice during its formation, and spectra produced by Fourier transformation show that its integrated intensity is <1% of the total absorption signal. At room temperature the occluded water is mobile, but as temperature is lowered the line broadens and eventually disappears under the main signal. CW derivative spectra, produced using a modulation width larger than the linewidth, cause the line to appear broader and more intense that it actually is. Glemser (*6*) assigned it to adsorbed water but Fripiat and Touillaux (*8*), who found that it was independent of surface area and remained after outgassing, assigned it to rotating OH_2^+ defects. The latter assignment would, however, involve 180° flips of the OH_2^+ about the Al–OH_2^+ line and, as the dipolar interaction is known to survive this motion (*18*), the corresponding spectrum would not be narrowed.

The well-resolved doublet lineshape shows that for each proton (hydrogen atom) in γ-AlOOH, one dipolar interaction is much stronger than the rest. This means that one proton is much closer than all the others in the sample, i.e., there are proton pairs. The doublet lineshape may be regarded as diagnostic for proton pairs and is typical for solids containing H_2O (such as gypsum, $CaSO_4 \cdot 2H_2O$, Ref. (*16*)), but for γ-AlOOH, because the IR absorption band at ca. 1600 cm^{-1} characteristic of OH_2 groups is not observed, it must arise from pairing of protons bonded to different oxygen atoms. In general, it is extremely difficult to determine the separation, R, between the protons in a pair with accuracy. R can, however, be estimated using a simple model given by Pake (*16*). The dipolar spectrum of an isolated proton pair would consist of two lines with separation δB where

$$\delta B = 2\alpha(1-3\cos^2\theta),$$

$$\alpha = \tfrac{3}{4}\gamma(\mu_0/4\pi)R^{-3},$$

and where θ is the angle between the interpair and static field vectors. The doublet lineshape in a powder is taken as the sum (of all such lines over all θ values) convoluted with a Gaussian broadening function of width β, which is meant to take account of the effects of all extra-pair interactions. The value $R = 1.69$ Å was calculated from the room-temperature derivative absorption spectrum using the fitting method of Gabuda *et al.* (*19*) with $\alpha = 4.40$ G and $\beta = 1.67$ G. For Pake's model, $M_2 = 4\alpha^2/5+\beta^2$ and the fit gives $M_2 = 18.3\ \mathrm{G}^2$, in good agreement with the value obtained by other methods. The effect of motions, such as vibrations, on lineshape is a complex problem and it is not obvious how corrections, such as have been made for R in crystal hydrates (*18*), could be made to our value for R in γ-AlOOH. The estimated $R = 1.69$ Å is much less than the distance between neighboring chains (2.87 Å) and the lineshape must therefore arise from interactions (and therefore pairs) within a single chain.

A model for γ-AlOOH which includes proton pairs can be proposed based on the zig-zag hydroxyl chain. A neutron diffraction study of the isostructural compound γ-FeOOH (*20*) was interpreted in terms of symmetrical H-bonds, but this arrangement is unlikely because the O . . . O distance of 2.70 Å (in both γ-AlOOH and γ-FeOOH) is far outside the range (2.40–2.50 Å) where these are known to occur. IR measurements (*10*) on γ-AlOOH indicate that the H-bonds are nonlinear, as is known to be the case in α-AlOOH (diaspore) which has a similar O . . . O distance (2.65 Å, Ref. (*21*)). Figures 3a and b illustrate average structures that might be observed by neutron diffraction if the protons could occupy one site (occupancy = 0.5) or two sites (occupancy = 0.25), respectively. Both models correspond to the space group *Cmcm* and the average arises from disorder between the arrangements in different chains and layers. Only the two-site model is consistent with the NMR absorption lineshape.

For the one-site model, the proton of a hydroxyl group in a given chain would have two others equidistant from it (Fig. 4a); there are therefore no proton pairs and the model is inconsistent with the NMR absorption lineshape. This is true for any deviation of the site off the O . . . O line, for symmetric H-bonds and for linear H-bonds, which have been assumed in previous NMR studies (*5, 7*).

For the two-site model, the arrangement in a given chain, or domain within it, could be as in Fig. 4b, which contains proton pairs. Assuming an O–H bond length of 1.0 Å, the heavy atom coordinates given by Milligan and McAtee (*3*) and the angle, θ, between the O–H and O . . . O vectors to be the same for both sites, $\theta = 10°$ gives $R = 1.70$ Å. Using van Vleck's formula, M_2 contributions of $18.6\ \mathrm{G}^2$ from protons in the same chain and $1.6\ \mathrm{G}^2$ from interactions with Al atoms

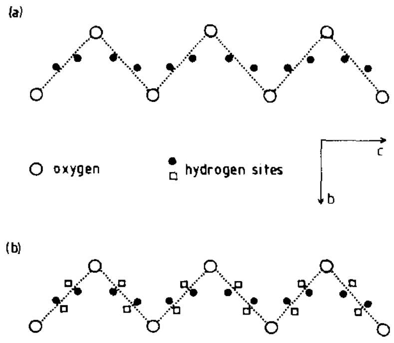

FIG. 3. Model average structures for the interlayer region in γ-AlOOH based on occupation of (a) one hydrogen site (occupancy = 0.5) and (b) two hydrogen sites (occupancy = 0.25). The hydrogen sites are all 8(*f*) sites in the space group *Cmcm*.

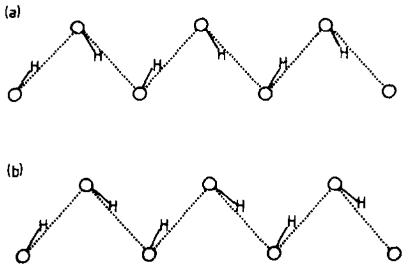

FIG. 4. Models of a single chain of hydroxyl groups in the interlayer region in γ-AlOOH corresponding to occupation of (a) one hydrogen site and (b) two hydrogen sites. Model (a) is inconsistent with the NMR absorption lineshape.

are calculated. The contribution from other chains, which is difficult to estimate because of possible disorders between them, is taken as 0.5 G^2, giving a total M_2 of 20.7 G^2. This value is slightly high but does not rule out a model of this sort. For instance, $\theta = 7°$ gives $M_2 = 18.2\ G^2$, which is in accord with experiment, and $R = 1.77$ Å.

Acknowledgments

We thank Bruker-Physik A.G. for the use of equipment at their Applications Laboratory. One of us (R.C.T.S.) thanks the Science Research Council for a research fellowship.

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