Proton Magnetic Resonance in Tincalconite

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From the proton magnetic resonance spectra of tincalconite recorded between —153⁰C and +80⁰C OH-groups and water molecules were established. By dehydration at 88⁰C over P_2O_5 in vacuum tincalconite loses three water molecules per formula unit with an amorphous rest. The proton resonance line-shape of this dehydration product corresponds to the OH-groups spectrum. The comparison of the experimental curve at low temperature with theoretical ones for two different ratios $OH:H_2O$ suggests $Na_2[B_4O_5(OH)_4] \cdot 3H_2O$ as the correct formula for tincalconite. The nature of the motion of the water molecules is discussed.

INTRODUCTION

Menzel[1] found that tincalconite loses three molecules of water of crystallization by dehydration at 88⁰C in vacuum giving an amorphous species. There is some similarity in the process and in the result of dehydration between tincalconite and borax. The latter compound has hydrogen both in OH-groups and H_2O molecules[2,3].

The proton magnetic resonance in tincalconite has been examined previously by Dharmati et al.[4] in a powdered sample. They found a narrow proton line, but resembling the doublet of a two-spin system. The authors assumed that the line due to water molecules undergoing rotational motion overlaps the proton line due to OH-groups which was of the same width.

From B^{11} resonance Dharmati et al.[4] and in particular Cuthbert and Petch[5,6] who made complete and precise measurements on a single crystal conclude that boron atoms in tincalconite have two unique sites in the unit cell with triangular and tetrahedral coordination. They are linked in closed-ring polyions. Such a picture of boron coordination is in agreement with the borax polyion and supports Christ's prediction[7] about the polyions to be found in crystals of the borax family.

The present PMR investigations were undertaken in order to determine the quantitative distribution of hydrogen nuclei in different groups with the view of resolving the contradiction between the suggested formula of tincalconite[4] and various experimental evidence. This should be of some help in determining the crystal structure of tincalconite, which is as yet unknown.

EXPERIMENTAL

Preparation of samples

The polycrystalline tincalconite was obtained by heating borax (Merck) at 60⁰C to constant weight. The final product gave the x-ray diagram characteristic of tincalconite[1].

The dehydrated sample was prepared by slow dehydration of the »pentahy-drate« at 88⁰C in a vacuum desiccator at a pressure of about 2 mm Hg. The attainment of constant weight took over one month and the water lost corresponded to slightly less than three molecules per formula unit.

Another dehydrated sample was obtained by heating tincalconite at 140⁰C, a temperature chosen after DTA and TGA-results. This sample also lost about three water molecules.

Apparatus

The broad — line magnetic resonance spectrometer used in this study was of a conventional bridge — type described previously[8].

The proton magnetic resonance absorption spectrum of tincalconite was inve-stigated over the temperature range +80⁰C to —153⁰C. The temperatures lower than —40⁰C were obtained by blowing a cold stream of nitrogen into the probe. For the higher temperatures a »Lauda« cryostat type UK70 was used. The accuracies of the given values are ±1⁰C for the lower and ±0.1⁰C for the higher temperature span.

<div align="center">RESULTS</div>

The variation of the observed second moment of the proton absorption spectrum over the temperature range studied is shown in Fig. 1. These second moments were obtained by numerical integration of the experimentally observed first derivatives and corrected for modulation broadening after Andrew's formula[9].
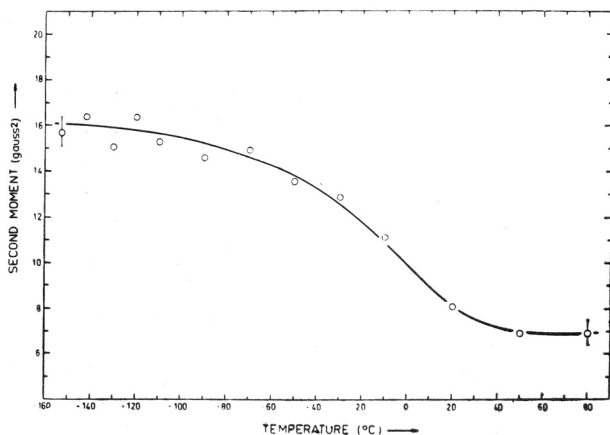

Fig. 1. Proton magnetic resonance second moment dependence on temperature in polycrystalline tincalconite.

We paid special attention to the calculation of the second moments because of a very pronounced tailing of the line shapes. Thus we used at least 10 and mainly 20 spectra for calculations at any given temperature. All these results were obtained with sufficiently small amplitude of modulation (1.6G—2.3G) in order to preserve the true line shapes.

Fig. 2. shows the change with temperature of the characteristic absorption first derivatives. Below —120⁰C all the spectra have the same shape, second moment and line width. The central line width is throughout at 7.90 G, while the broader line of 13.5 G width appears below —120⁰C.
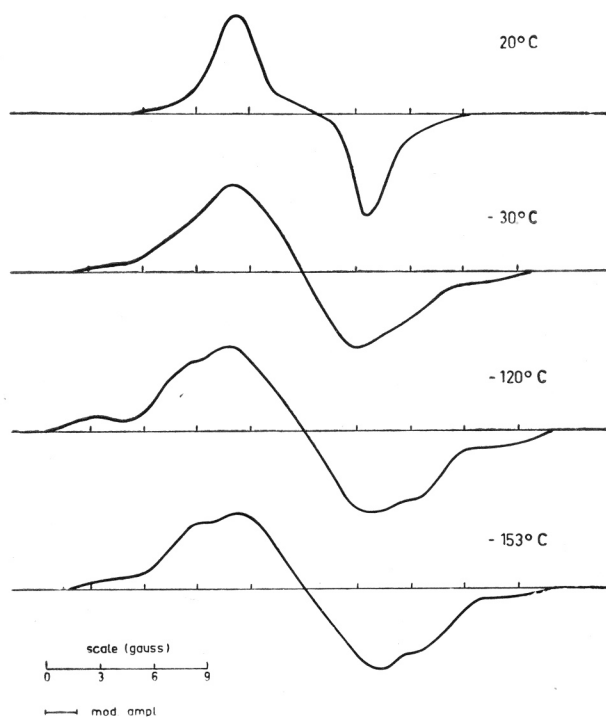
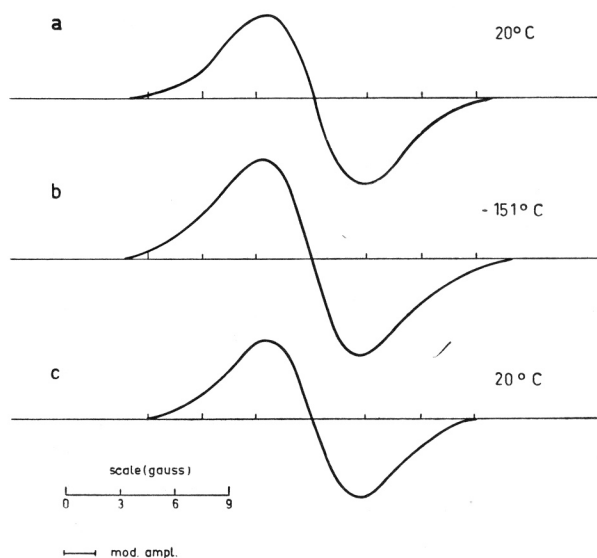Fig. 2. Proton magnetic resonance spectra of tincalconite at different temperatures.

Fig. 3. P. m. r. spectra of tincalconite dehydrated at 88⁰C over P₂O₅ (a and b) and
at 140⁰C (c).

The spectra of the dehydrated samples given in Fig. 3. are the same irrespective of the temperature. The low temperature second moment is 6.3 G^2.

<center>DISCUSSION</center>

In Menzel's[1] isobaric dehydration of tincalconite there is an amorphous species corresponding to the loss of three water molecules per formula unit of the original sample. Such a phase is similar to the residue after dehydration of borax, in which the remaining »water molecules« are bound as OH-groups in the polyions that form part of the structure[10].

Dharmatti et al.[4] found that hydrates of sodium tetraborate all have similar B^{11} resonance. On the other hand they conclude from the proton magnetic resonance spectrum at room temperature that the molecular formula of tincalconite may be Na$_2$[B$_4$O$_6$(OH)$_2$] · 4 H$_2$O. It has already been pointed out by Cuthbert and Petch[6] that this interpretation is incorrect. Our dehydration over P$_2$O$_5$ at 88^{0}C gave the same result as the one obtained by Menzel[1]. In order to confirm further the presence of two different types of »water of crystallization« in tincalconite we have done the thermal gravimetric analysis. At 150^{0}C there is a sharp loss corresponding to three H$_2$O per formula unit with a subsequent continuous loss in a wide temperature interval from 150^{0}C—720^{0}C. Loss of three water molecules results in an amorphous species. These results of dehydration suggest strongly that there are two kinds of »crystallization water« in tincalconite. As tincalconite can be prepared by heating borax at 60^{0}C there is no pressing reason for any change of the anionic part of the borax structure, and thus it is very likely that the two H$_2$O molecules remaining after dehydrating tincalconite are also bound as OH-groups.

The number of unique sites, the coordination of sites (triangular and tetrahedral) and the symmetry of the polyion are the same in tincalconite and in borax[5].

On crystallochemical grounds Christ[7] predicts the borax — type polyion in tincalconite and direct confirmation in this respect may be found in the results of proton magnetic resonance.

Though the observed proton resonance spectrum of tincalconite at room temperature may roughly correspond to a two-spin system, the spectra observed at lower temperatures show, however, important change in the line shape and second moment (Figs. 1. and 2.). It can be concluded also from this line-shape that protons in tincalconite are in two different magnetic enviroments. The broad line is characteristic of protons in water molecules as encountered thus far in numerous hydrates. The narrow line can be expected if the protons are in relatively isolated OH-groups. Its width appears to be the same as at room temperature and the overlapping at room temperature with the spectrum of mobile water molecules is thus confirmed, though we disagree with the final conclusion of Dharmatti et al.[4] regarding the structural formula.

The spectra of two dehydrated samples of tincalconite are characteristic of OH-groups (Fig. 3.) with the line width of 6.3 G. This line width is the same as in the amorphous residue of borax[10].

In order to define the structural formula of tincalconite theoretical H$_2$O-curves were matched to the experimental one recorded at —153^{0}C. (An

interproton distance of 1.58 Å and a broadening parameter $\beta = 1.54\,\mathrm{G}$ were assumed. Such values are usually encountered in hydrates).

Curve 2 in Fig. 4. was drawn according to the ratio $2\,\mathrm{OH} : 4\,\mathrm{H_2O}$ as required by the formula in reference 4. Evidently, there is a serious mismatch
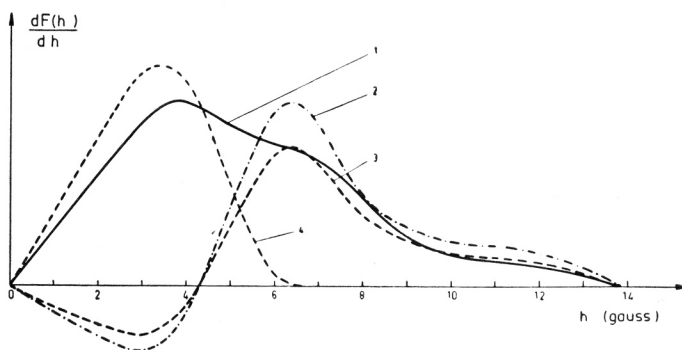

Fig. 4. P. m. r. derivative curves at —153⁰C
—————— (1) observed spectrum of tincalconite
—.—.—. (2) calculated spectrum of the water of crystallization for the ratio $2\,\mathrm{OH} : 4\,\mathrm{H_2O}$
- - - - - (3) calculated spectrum of the water of crystallization for the ratio $4\,\mathrm{OH} : 3\,\mathrm{H_2O}$
- - - - - (4) the spectrum of OH-groups according to the last ratio.

with the $\mathrm{H_2O}$-part of the experimental curve (1). Thus, the formula $\mathrm{Na_2[B_4O_6(OH)_2]} \cdot 4\,\mathrm{H_2O}$ cannot be accepted because it violates both the boron — and proton — magnetic resonance results, though it satisfies the formal stoichiometry.

On the other hand, this last requirement cannot be fulfilled with the polyion $\mathrm{[B_4O_7(OH)_2]^{2-}}$, see ref. 6, (in spite of the fact that it is in agreement with the boron resonance evidence) so that there was no need for further proton — resonance curve — matching.

If we suppose the same anion as in borax, $\mathrm{[B_4O_5(OH)_4]^{2-}}$, and three molecules of water of crystallization as indicated by the dehydration data, than the theoretical $\mathrm{H_2O}$-line (3 in Fig. 4.) is in good agreement with the experiment. The correct structural formula, $\mathrm{Na_2[B_4O_5(OH)_4]} \cdot 3\,\mathrm{H_2O}$, is in agreement with all the available experimental evidence: stoichiometry, dehydration, boron — and proton — magnetic resonance. Hence, tincalconite is neither a pentahydrate as accepted so far by its chemical formula, nor is a tetrahydrate as suggested by Dharmatti et al.[4], but is a trihydrate, as was predicted by Christ[7]. A reasonable curve fitting is obtained also for the room temperature results using the trihydrate formula.

It is evident from the proton magnetic resonance spectra that the water molecules are very mobile and their line overlaps at room temperature the spectrum due to the OH-groups. We suppose the direction of motion to be about an axis perpendicular to the interproton vector of the water molecule. The high temperature second moment of tincalconite can be calculated as follows:

$$S_{HT} = x S_{(OH)} + (1-x)\,\frac{S_{LT\,(H_2O)}}{4} \tag{1}$$

where x is the fraction of protons in OH-groups, $S_{(OH)}$ is the second moment due to these protons, and $S_{LT\,(H_2O)}$ is the second moment of the water of crystallization at low temperature. If unhindered rotation of water molecules occurs in the way mentioned above, the second moment at room temperature is 1/4 of the rigid lattice second moment, which from our experimental spectra is 24 G^2.

With $S_{(OH)} = 5.0$ G^2 (which very likely does not change significantly with temperature), Eq. 1 results in 5.6 G^2 hile the observed value is 6.9 G^2 at 80⁰C. This difference may be explained by some kind of hindered rotation of water molecules — an observation found also in borax[3]. Tincalconite differs from borax in that there is no motion of OH-groups which was established in borax[3].

On the other hand there is another difference between borax and tincalconite. While the OH-line is much broader in the amorphous phase than in the crystalline borax, in tincalconite the »amorphous line« is narrower than the original OH-line.

The energy of activation for the H_2O-reorientation process was calculated from the second moment data using this formula[11]:

$$\tau = \frac{tg\left(\dfrac{II}{2} \cdot \dfrac{S_T - S_{HT}}{S_{LT} - S_{HT}}\right)}{\alpha \cdot S_T^{1/2}} \qquad (2)$$

Where S_{LT} and S_{HT} refer to the low- and high-temperature limits of second moment, S_T is the second moment observed at temperature T, and α is the line-shape parameter of the order of unity. Correlation times were calculated and a plot of ln τ vs. 1/T gives a straight line and an activation energy of 3.42 kcal/mol. Such determination of activation energy from second moments is liable to appreciable error. By using Waugh's[12] formulation $E_a \sim 37$ T where T is the temperature at which the line width transition takes place, we get 5.25 kcal/mol. This energy of a few kcal/mol is of the right order of magnitude, similar to that obtained for the reorientation mechanism in borax[3].

REFERENCES

1. H. M e n z e l, Z. anorg. allg. Chem. **224** (1935) 1.
2. N. M o r i m o t o, Miner. J. **2** (1956) 1.
3. S. M a r i č i ć, M. P i n t a r, and Z. V e k s l i, J. Phys. Chem. Solids **23** (1962) 743.
4. S. S. D h a r m a t t i, S. A. I y e r, and R. V i j a y a r a g h a v a n, J. Phys. Soc. Japan **17** (1962) 1736).
5. J. D. C u t h b e r t and H. E. P e t c h, J. Chem. Phys. **38** (1963) 1912.
6. J. D. C u t h b e r t and H. E. P e t c h, J. Chem. Phys. **39** (1963) 1247.
7. C. L. C h r i s t, Am. Mineralogist **45** (1960) 334.
8. S. M a r i č i ć, V. P r a v d i ć, and Z. V e k s l i, Croat. Chem. Acta **33** (1961) 187.
9. E. R. A n d r e w, Phys. Rev. **91** (1953) 425.
10. A. B e z j a k, I. J e l e n i ć, S. M a r i č i ć, and Z. M e i ć, Croat. Chem. Acta **35** (1963) 295.

11. G. R. M u r r a y, Jr. and J. S. W a u g h, *J. Chem. Phys.* **29** (1958) 207.
12. J. S. W a u g h, *Lectures of Solid State Physics*, Hercegnovi, 1963, p. 70.

IZVOD

Protonska magnetska rezonancija u tinkalkonitu

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Na osnovu spektara protonske magnetske rezonancije tinkalkonita ($Na_2B_4O_7 \cdot 5H_2O$), snimanih u temperaturnom intervalu od —153⁰C do +80⁰C, ustanovljeno je postojanje hidroksilnih skupina i kristalizacijske vode. Dehidratacijom iznad P_2O_5 kod 88⁰C u vakuumu gube se tri mola vode po jediničnoj formuli dok amorfni ostatak daje spektre karakteristične za OH-grupu. Uspoređivanjem eksperimentalnih spektara kod niskih temperatura s teoretskima, računatim sa dva moguća omjera $OH \cdot H_2O$ određeno je da je formula tinkalkonita $Na_2B_4O_5(OH)_4 \cdot 3H_2O$.

Studirana je priroda molekularnog kretanja kristalizacione vode kojih linija kod sobne temperature prekriva spektar hidroksilnih skupina.

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