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# A Proton Magnetic Resonance and Infrared Study of Colemanite and Inyoite*

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A proton magnetic resonance and IR investigation of colemanite, $CaB_3O_4(OH)_3 \cdot H_2O$ and inyoite, $CaB_3O_3(OH)_5 \cdot 4H_2O$, is in agreement with the X-ray crystal structure analysis[1,2] concerning these two newly proposed formulae. It is confirmed that at room temperature there is a dynamic distribution of proton sites in the ferroelectric colemanite, while there is no such effect in inyoite. There are two second moment transitions in p. m. r. spectra of colemanite. The one at about —110°C is due to the onset of reorientation of water molecules. The second one at $T_c$ is discussed in terms of a dynamic model involving a change from a symmetric double well potential for the moving protons into an asymmetric one below $T_c$.

## INTRODUCTION

A series of borate minerals of general composition $2CaO \cdot 3B_2O_3 \cdot xH_2O$, with x = 13, 9, 7 and 5, has attracted interest of X-ray crystallographers. Christ, Clark and Evans[1] have recently elucidated the crystal structure of colemanite (x = 5) by three-dimensional Fourier synthesis, while Joan R. Clark[2] solved that of inyoite (x = 13). The coordinates of all atoms except those of hydrogens are determined and new formulae proposed: $CaB_3O_4(OH)_3 \cdot H_2O$ for colemanite and $CaB_3O_3(OH)_5 \cdot 4H_2O$ for inyoite.

Of the two minerals colemanite is particularly important in view of its piezo-[3], pyro[3,4], and ferroelectricity[5,6]. None of these effects are known to occur with inyoite. The ferroelectric Curie point of the former compound is at about —7°C, depending on admixtures[6]. The loss of the centre of symmetry connected with this transition and verified by quadrupole perturbed NMR spectra of boron[7] has led the authors of the crystal structure of colemanite to postulate a dynamic rather than statistically static distribution of hydrogen sites above the Curie point. The positions of hydrogen atoms were inferred from the known O—O distances and from the rest of the structure which consists of chains made up of B—O tetrahedra and triangles. No such disorder of hydrogen sites is expected in inyoite at room temperature[2].

It occurred to us that the present knowledge of complete crystal structures of these two minerals makes it worthwhile to undertake a combined proton magnetic resonance and infrared study. It was hoped to confirm independently

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the formulae proposed by C. L. Christ *et al.*[1] and J. R. Clark[2]. We also aimed at obtaining additional information concerning the different role of hydrogen atoms in the two minerals which would help to correlate in some way the hydrogen bond system in colemanite with its ferroelectric behaviour.

## EXPERIMENTAL

### *Samples*

Colemanite was kindly given to us by Dr. Lj. Barić of The University of Zagreb, and it is of Turkish origin — Aceb/Iskeleköy, Anatolia. From a rather large piece of polycrystalline material pure small crystals were carefully selected and powdered.

The same procedure was used for inyoite, a sample of which we obtained from the U. S. National Museum through the very kind help of Dr. C. L. Christ of the U. S. Geological Survey. The sample comes from Argentina.

### *Apparatus*

The NMR equipment was of the usual PKW-type with a rather high level of oscillation. This introduced serious difficulties in taking proton-resonance spectra at low temperatures, particularly of inyoite which seems to have much longer relaxation time than colemanite. The spectra were taken in a field of 3600 gauss.

The low temperature device was described earlier[8]. The temperatures given here are accurate to within ± 2°C.

The IR spectrometer was a Perkin-Elmer 21 double beam model.

## RESULTS AND DISCUSSION

### *A. The »rigid« structures*

In spite of some 150 NMR spectra recorded the results have rather large standard deviations due to the above mentioned difficulties. Some representative first derivatives of absorption lines at different temperatures are given in Fig. 1 for both colemanite and inyoite.

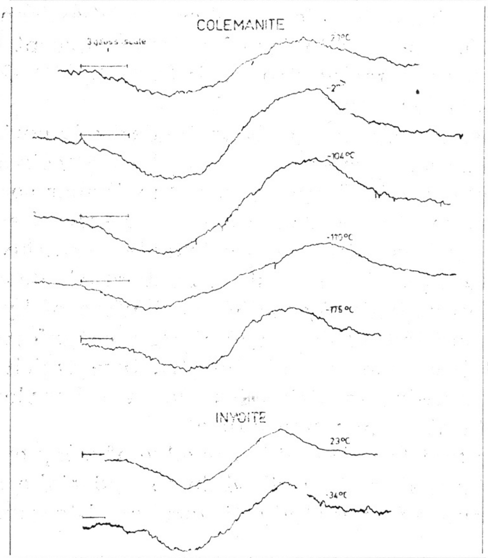
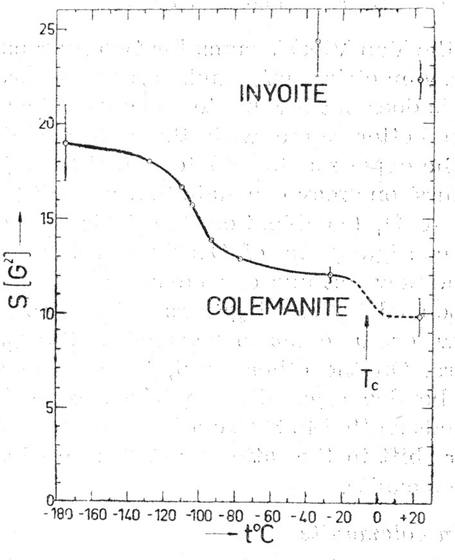


Fig. 1. Proton magnetic resonance spectra of colemanite and inyoite at different temperatures.

Although at this stage we did not make any quantitative analysis of the line shapes, one can easily note a few characteristic points in a qualitative way. In both cases a combination of a two-spin line with a narrow component is to be expected. However, the fine detail in the middle of the lines appears to be lost due to large intermolecular broadening. This is plausible if we take into account that there are several interproton distances between adjacent hydroxyls of about 2 Å. Nevertheless, the characteristic tail of a two-spin curve seems to have been preserved, and in the middle of all lines a faint narrow component can be seen.

The second moment dependence on temperature is shown in Fig. 2. While there are enough experimental points for colemanite to locate two transitions*, we have only two points for inyoite because measurements at lower temperatures proved to be useless owing to saturation.



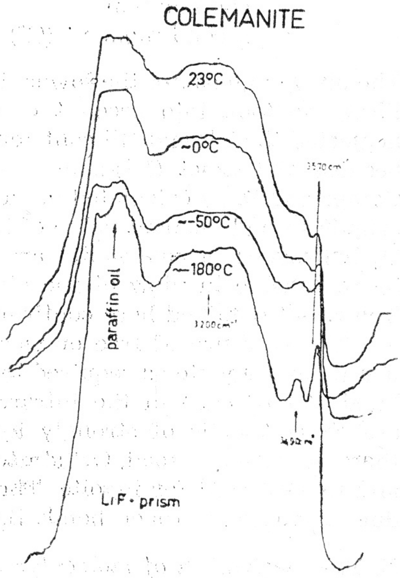


Fig. 2. Second moment dependence on temperature for colemanite and inyoite.
Fig. 3. Infrared spectra of colemanite at different temperatures.

An approximate calculation of the »rigid« second moment for inyoite, by assuming 1.58 Å interproton distance in water molecules and the new formula proposed by Clark$^2$, is in reasonable agreement with the experimental values. This also implies that Clark$^2$ is right in concluding that there is no dynamic disorder of proton sites in inyoite. In case there is any, the frequency of such movements should be less than some 55 Kc/s. As for a change of about 2 gauss$^2$ between room temperature and —34°C, it might well be caused by librational motion of the water molecules. Further experiments in this direction are in progress.

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* We are grateful to one of the referees for drawing our attention to the article of Holuj and Petch (ref. 10), whose results confirm the existence of these two transitions.

We shall now discuss the low-temperature or the »rigid« structure of colemanite.

There is one point left open from the crystal structure analysis. It concerns the position of the $O_6$ hydroxyl proton in the ferroelectric phase. According to Christ *et al.*[1], after the centre of symmetry has been destroyed by freezing the system below the Curie point, the mentioned proton may become permanently bonded to either $O_1$ or $O_3$. This would be plausible owing to similarity of the two corresponding hydrogen bond lengths. We checked this point by calculating the second moment values for the four possible alternatives. We denote the cases where the protons of both $O_6$ hydroxyls of an asymmetric unit (in the acentric ferroelectric cell) point to the same oxygen by 1,1 and 3,3, respectively; the 1,3 and 3,1 notations correspond to a 50 : 50 distribution between the two sites, and the results are as follows:

| combination | 1,1 | 1,3 | 3,1 | 3,3 |
|---|---|---|---|---|
| second moment ($G^2$) | 16.7 | 23.0 | 30.8 | 37.1 |

The above values are the lower limits to the Van Vleck's sums for two reasons. First, we took into account only one asymmetric unit, and, secondly, we neglected the $B^{10}$ and $B^{11}$ contribution. This does not invalidate our conclusions, because the exact (1,1)-sum would even better agree with the experiment. Comparing these calculated values with the experimentally determined (Fig. 2) »rigid« second moment value of 19 ± 2 gauss$^2$ one may conclude that at —175°C $O_6$ hydrogens in colemanite are bonded to $O_1$ (combination 1,1). This would be reasonable in view of the electronic configurations of O's discussed later. The result obtained here confirms also the new formula of colemanite.

The presence of free or weakly H-bonded hydroxyl groups both in colemanite and inyoite as required by the new formulae is also revealed by the $\nu_{OH}$ band at 3570 cm$^{-1}$ in the infrared spectra. On the other hand, these spectra are characteristic of strongly hydrogen bonded crystalline hydrates as well: there are strong, broad, OH stretching bands shifted to 3200 cm$^{-1}$ for colemanite and to 3420 cm$^{-1}$ for inyoite. The smaller shift in the latter crystal is possible due to longer hydrogen bonds than in colemanite.

### *B. The mechanism of molecular motion in colemanite*

The second moment dependence on temperature (Fig. 2) for colemanite proves that the distribution of hydrogen sites at room temperature is dynamic. We can also find support for this from the temperature dependence of the colemanite IR spectra. The static model of ferroelectric transitions in crystals with hydrogen bonds requires changes in O—H distances of as much as 0.1 Å. The corresponding OH stretching frequency shift should be of the order of at least 100 wave numbers. As it can be seen from Fig. 3 there is no such shift after cooling below $T_c$, and if there is any at all it is of the order of some 20 cm$^{-1}$. This can well be understood on the basis of a dynamic model after which there is no appreciable change in the O—H distances below $T_c$, while only the two potential minima for protons become asymmetric.

In discussing the possible mechanism of molecular motion underlying the double transition in colemanite we start with the scheme proposed by Christ *et al.*[1] Fig. 4 depicts the ferroelectric arrangement of water molecules and hydroxyls which take part in hydrogen bonding of neighbouring B—O chains.

Only oxygens linked together by hydrogens are shown for the sake of simplicity. Such a configuration is meant to exist below the Curie point after the centre of symmetry has been destroyed.[1] In fact, this »rigid« structure seems to be possible only far below $T_c$ (at —175°C), as revealed by second moment calculations given in section A.

We now suppose that on raising the temperature from —175°C molecules of water preserve the $O_8$—H . . . $O_7$ link (which is shorter than $O_8$—$O_6$) to the rest of the structure. At the same time they start reorienting around an axis identical with that of the hydrogen bond. In the final consequence, at room temperature, the second hydrogen of a water molecule becomes a half-time contributor[1] to $O_8$—$O_6$ and $O_8$—$O_8$ hydrogen bonds. This implies a symmetrical double well potential for the water molecules at room temperature and the centre of symmetry is thus preserved. However, we are in doubt whether the supposed (Christ *et al.*[1]) half time $O_6$-hydrogen can be reconciled with the electronic configuration of the neighbouring $O_1$ and $O_3$. Whatever their electronic state (either $sp^2$ or $sp^3$) the lone pair electron projection is more favourable to create a hydrogen bond $O_6$—H . . . $O_1$, which is also shorter (2.80 Å) by 0.1 Å than $O_6$—$O_3$ distance. Such a localization of the $O_6$-hydrogen does not interfere with the requirement for a centre of symmetry in the paraelectric state. In other words, there is no need for the $O_6$ hydrogen to have a symmetrical potential well above $T_c$ in order to preserve the centre of symmetry.

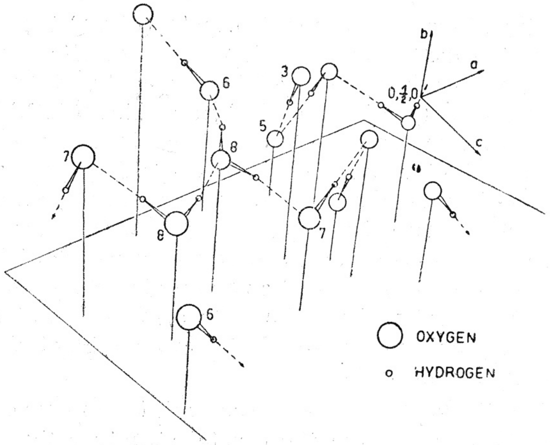

Fig. 4. The hydrogen bond network in colemanite at —175° C [after Christ, Clark, and Evans, *Acta Cryst.* **11** (1958) 761, except for localizing the $O_6$-$O_1$ hydrogen along the $O_6$-$O_1$ line]. Only oxygens linked by hydrogens are shown for the sake of simplicity. The B—O chains run parallel on either side of this hydrogen bond system.

We are concerned in Fig. 4 with the two water molecules ($O_8$) and two hydroxyls ($O_6$). There is little doubt that this pair of water molecules should reorient cooperatively due to serious steric hindrance if the two hydrogens face each other along the $O_8$—$O_8$ line.

We shall try to reconcile the above facts and assumptions with the double NMR transition in colemanite as shown in Fig. 2.

The described model for the motion of water molecules means a reorientation around the $O_8$—$O_7$ bond. The interproton vector is inclined at $37.5^0$ in respect to the reorientation axis. Without detailed knowledge of the shape of the potential field, which is asymmetric below $T_c$, and without the knowledge of the potential barrier height no accurate calculation for the reduction of second moment can be made. However, an upper limit for the change of the second moment at the low temperature transition is obtained by assuming that the reorientation mechanism is simple free rotation. The reduction factor[9] is then 0.20. If we neglect the change in intermolecular broadening the experimentally found change in second moment of 7 $G^2$ (between —175 and —$60^0$C) would correspond to a »rigid« water molecule second moment of 22 $G^2$. (This result has been obtained, of course, by applying 2/5 ratio for the water protons according to the new formula.) The last value yields an interproton distance of some 1.59 Å, which is reasonable. However, it must be taken with definite caution due to the large experimental error and the simplification introduced into the calculation.

As for the change in second moment near $T_c$ (Fig. 2) there is no doubt it is a transition and not a continuous effect. Similar results have been obtained in our Laboratory with other ferroelectrics having hydrogen bonds: (glycine)$_3$ $H_2SO_4$, (glycine)$_3$ $H_2SeO_4$, (glycine)$_3$ $H_2BeF_4$, and $NaH_3(SeO_3)_2$. This particular transition has also been verified more thoroughly by Holuj and Petch[10]*. They consider it to be due to the onset of $O_6$-hydroxyl reorientation while water molecules have already started moving at much lower temperature (—$110^0$C). Their interpretation implies different reorientation frequencies for the water molecule protons and $O_6$-proton, and consequently different longitudinal relaxation times. The two components of the proton absorption curve should therefore show different saturation behaviour. In some relevant measurements of this work no such effect was observed, but a systematic study of saturation at different temperatures is desirable.

This means that, if the $O_6$-hydroxyls reorient, they move cooperatively with the water protons. It follows from the crystal structure that such a combined movement is not coplanar. This case has not yet been treated and before the appropriate second moment reduction factor is calculated, this possibility cannot be definitely disproved.

However, as discussed above, at present we cannot see any strong evidence for the necessity of $O_6$-hydroxyl reorientation. The $T_c$ proton magnetic resonance transition cannot be due to the onset of any particular reorientation of the protons, because the water molecules are moving above as well as below $T_c$ and if the $O_6$-hydroxyls move, they move with the same frequency as the water molecules. On the other hand, Holuj and Petch[10] have proved that definite rearrangement of the B—O part of the structure takes place at $T_c$, and we are also of the opinion that it is the ordering of hydrogen bonds that triggers this transition. The point we differ in is that this »ordering« is of a dynamic cooperative nature, *i. e.* the net polarization of the crystal lattice is produced by a

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* Their second moment values are about twice as large as ours. We attribute this to the fact that they used a single crystal, but unfortunately there is no specification concerning the particular orientation at which the spectra were taken.

change in shape of the double well potential for water protons, which is symmetric above $T_c$ and asymmetric below $T_c$. Of course, the induced dipole moments — rearrangement of the B—O network — also contribute to the spontaneous polarization.

As soon as the shape of the double well potential for the water protons becomes asymmetric, the induced rearrangement of boron sites would certainly change to some extent the total second moment. It is likely that the difference in the average positions of the reorienting water molecule protons below and above $T_c$ would change the intermolecular contribution as well and therefore add its part to the change of the total second moment at $T_c$.

The present work cannot distinguish whether $O_6$ protons move simultaneously with water molecules, or they do not move at all. This is irrelevant to drawing the conclusion from the above consideration that the ferroelectric transition is produced by dynamic ordering of protons in hydrogen bonds, while the proton magnetic resonance $T_c$-transition is due to the change of the intermolecular second moment.

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## IZVOD

### Ispitivanje kolemanita i inioita protonskom magnetskom rezonancijom i infracrvenom spektroskopijom

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Ova su ispitivanja u suglasnosti s rentgenografskim analizama kristalnih struktura kolemanita i inioita[1,2] u pogledu njihovih formula $CaB_3O_4(OH)_3 \cdot H_2O$ odnosno $CaB_3O_3(OH)_5 \cdot 4H_2O$. Potvrđeno je također, da u feroelektriku kolemanitu postoji dinamička raspodjela položaja protona kod sobne temperature, dok toga nema u inioitu. Nađena su dva prijelaza u veličini drugog momenta za kolemanit: prvi, kod oko —110°C nastaje zbog reorijentacije molekule vode; drugi, kod $T_c$, diskutira se na bazi dinamičkog modela, koji uključuje promjenu od simetričnog dvostrukog potencijalnog minimuma u asimetrični ispod $T_c$.

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