THE PHONON SPECTRA OF BARIUM DIHYDROGEN PHOSPHATE

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The phonon frequency distributions in antiferroelectric $Ba(H_2PO_4)_2$ have been measured above and below transition temperature (133 K). Measurements have been performed by inelastic incoherent scattering of thermal neutrons using the beryllium detector method. Our purpose was to determine relations between the energy levels of phonons corresponding to the vibrations of hydrogen and the heavy part (PO_4 group) by using the analogy with the spectra of ferroelectric potassium dihydrogen phosphate where these relations were known.

It was found in our Laboratory that $Ba(H_2PO_4)_2$ was antiferroelectric and its crystal structure was determined. It was discovered that there were hydrogen bonds with five different distances O-O. Only two symmetric shorter bonds can make hydrogen oscillate between two potential minima in the direction of the bond. That means that only one fourth of all hydrogen atoms can make the effect which exists at KH_2PO_4. This may be the reason why the temperature dielectric anomaly, for example, is much weaker; its shape is similar to that of $NH_4H_2PO_4$-typical antiferroelectric.

Now we are going to compare our results (Fig.1) with the well-known spectra of KH_2PO_4.* It is obvious that they have similar shapes. The relations between the high energy peaks are complicated in both cases at both temperatures, and we will not discuss them here. However, it can be seen that the high energy part in $Ba(H_2PO_4)_2$ is

* M. Živanović, Doctor thesis, Faculty of Sciences, Beograd 1969.

translated to the left for about 30 meV.

We are going to discuss the distributions at room temperature at first. It is well known that the peaks between 50 meV and 70 meV correspond to O-H-O bond at which hydrogen oscillates between the two minima. The hydrogen peak in the spectrum of KH_2PO_4 is at 56.8 meV and it is higher than the one of heavy part at 66.5 meV. The similar relations are between the low energy peaks - the peak at 25.6 meV corresponds to hydrogen and that one at 31.7 meV to the heavy part. There are two peaks in the middle energy part of the $Ba(H_2PO_4)_2$ spectrum and they are at about 55 meV and 65 meV. The first analogically corresponds to hydrogen which oscillates between two minima, and the second one to the heavy atoms. They are

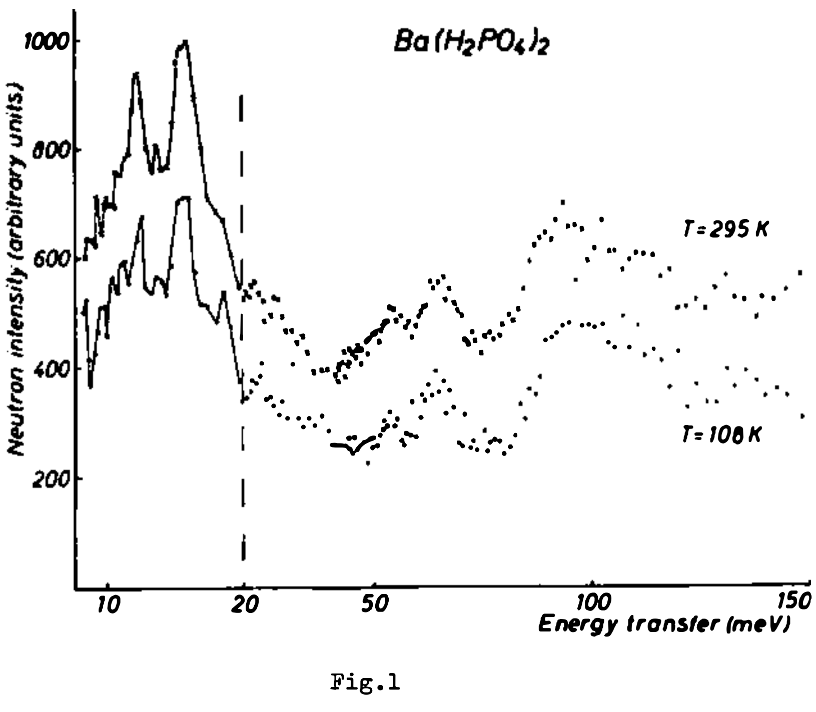

Fig.1

similar to those in the KH_2PO_4 spectrum, but here, the peak of the heavy part is more occupied than that of hydrogen. The low energy peaks are between 10 meV and 20meV, that is, they are shifted to the left.

The low energy peaks in KH_2PO_4 spectrum, below transition temperature, are joined in one, and the middle energy peaks are closer to each other. We notice that these peaks in the $Ba(H_2PO_4)_2$ spectrum are very slightly shifted one towards another in either energy range. In the low energy part changes are concentrated at about 10 meV.

Conclusion

The existence of hydrogen bond in which hydrogen oscillates between two potential minima, in the direction of the bond, has been shown (the same energy band as in KH_2PO_4). The number of hydrogen bonds of this type is smaller in $Ba(H_2PO_4)_2$ than in KH_2PO_4, and that is why the phonon peaks of heavy atoms are more occupied than these of hydrogen. The existence of three bonds in which hydrogen vibrates in one potential minimum likely causes the shifting of low and high energy groups of peaks towards low energies.