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2006 J. Phys.: Condens. Matter 18 6431

(http://iopscience.iop.org/0953-8984/18/27/N02)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **18** (2006) 6431–6432 doi:10.1088/0953-8984/18/27/N02

REPLY

Reply to Comment on 'Collective dynamics in crystalline polymorphs of $ZnCl_2$: potential modelling and inelastic neutron scattering study'

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Received 23 February 2006, in final form 19 April 2006
Published 23 June 2006
Online at stacks.iop.org/JPhysCM/18/6431

In their Comment, Kalampounias *et al* have suggested that the sample of α-$ZnCl_2$ prepared by us [1] may contain H_2O.

Our claim to refute this suggestion is through the diffraction and inelastic scattering measurements that we carried out on our sample using neutrons [2, 3], a probe known for its extreme sensitivity to hydrogen (the total scattering cross section for hydrogen is 82 b as compared to 4 b for Zn and 17 b for Cl). Signatures of the presence of hydrogen (if any, even in the form of water) would be predominantly visible both in the neutron diffraction pattern and in the inelastic neutron scattering spectrum.

We carried out a standard Rietveld refinement analysis on the neutron diffraction pattern of our sample, and we find (as shown in figure 1) that it conforms to the tetragonal structure of α-$ZnCl_2$ as reported in the paper by Brehler [4], with a χ^2 of 3.5, while this same pattern does not fit (as shown in figure 1) to the orthorhombic structure of δ-$ZnCl_2$ [5]. Any change in the stoichiometry of the compound (for example, the presence of bound water molecules) would have been clearly reflected in the intensities of the various Bragg reflections. Further, the presence of free water molecules would have led to very large background scattering in the diffraction pattern. This background scattering would have arisen from the large incoherent scattering cross section (80 b) of hydrogen. However, we observe that in our experiment, the observed background is within 2% of the estimated value with respect to that from a standard sample of nickel (with an incoherent scattering cross section of 5 b), for the same spectrometer.

Further, the neutron-weighted phonon density of states, as measured [1] for our sample for the range of energy transfer up to 60 meV, does not show any of the known peaks (for example, at around 6 and 25 meV) of the vibrations of water molecules [3].

Both of these observations hence rule out the presence of a significant amount of water in our sample, either in the crystalline lattice or in the form of free water molecules.

Acknowledgments

The authors wish to thank P S R Krishna and A B Shinde for useful discussions.

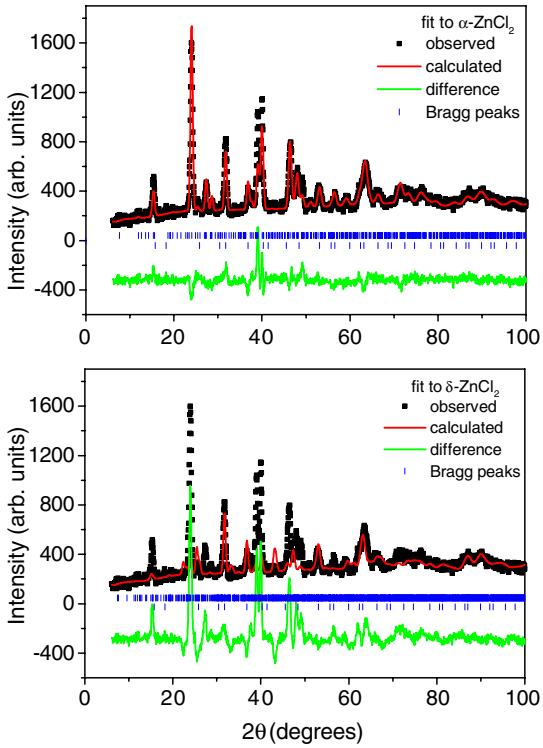

Figure 1. Rietveld fits of the observed diffraction pattern of our polycrystalline sample of $ZnCl_2$ to the reported structures [4, 5] of the α and δ phases. A two-phase analysis (with aluminium as the second phase) was done as the sample was contained in an aluminium sample holder.

(This figure is in colour only in the electronic version)

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