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COMMENT

Comment on 'Collective dynamics in crystalline polymorphs of $ZnCl_2$: potential modelling and inelastic neutron scattering study' by A Sen, Mala N Rao, R Mittal and S L Chaplot 2005 *J. Phys.: Condens. Matter* 17 6179

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In the above paper Sen *et al* formulate an interatomic potential applied to the '*four* crystalline polymorphs' (α-, β-, γ- and δ-type) of $ZnCl_2$. They also state in section 2 that Brynestad and Yakel have shown [1, 2] that the only existing pure anhydrous form is orthorhombic δ-$ZnCl_2$. In other words there is only one crystalline modification of the chemical compound with stoichiometry 1 Zn:2 Cl. The results of Brynestad and Yakel were verified in a recent *in situ* temperature dependent Raman study of the anhydrous salt where it was shown that from $-196\,^{\circ}C$ to the melting point there is only one crystalline form present, that of δ-$ZnCl_2$ ([3], figure 2 and table I). Furthermore, it was shown by means of *in situ* measurements that the hydrated $ZnCl_2$ crystals, referred to in the literature as γ-$ZnCl_2(xH_2O)$, transform above $100\,^{\circ}C$ to α-$ZnCl_2(yH_2O)$ with $y < x$ and finally above $200\,^{\circ}C$ anhydrous δ-$ZnCl_2$ is formed ([3], figure 3). Obviously, the solid prepared by Sen *et al* 'dried for a period of 8 h' is α-$ZnCl_2(yH_2O)$.

The degree of hydration of $ZnCl_2$ (the x and y values) is not known. However, during the above *in situ* Raman experiments an estimation of the liquid water volume condensed on the reaction tube outside the furnace was possible (see the experimental details in [3]). Thus, the water content of γ-$ZnCl_2(xH_2O)$ and α-$ZnCl_2(yH_2O)$ was measured to be approximately 8–12 and 4–6 wt%, respectively. This implies that the per mole content of H_2O is rather high, ranging from 50 to 70 mol% for the γ-form and 25–40 mol% for the α-form. Like for the hydrated first row transition metal halides the water molecules are bound through the oxygen to the central cation and determine the stoichiometry and properties of the compounds. The authors also state in section 2 that rapid cooling of molten $ZnCl_2$ or devitrification of the glass produces the α-phase while slow cooling of the melts favours the formation of the β-phase. This statement is not correct. In our long experience in preparing and handling zinc chloride, e.g. in [3–5], we have documented that anhydrous and oxide free (ZnO) melts prepared by either

hydrochlorination and filtering of molten $ZnCl_2$ or by melting the pre-sublimed crystalline δ-phase yield always, and independently of the cooling rate, a stable $ZnCl_2$ glass. Devitrification occurs only by bringing the glass to temperatures near 170 °C where the only crystalline form obtained is the anhydrous δ-phase. We have prepared glasses by these methods which have been placed in sealed Pyrex containers and remained at room temperature as glasses in our laboratory for years.

In conclusion, the analysis of the scattering experiments (Raman, x-ray and neutron) presented in tables 3, 4, 5, 7, 8 and 9 of the paper by Sen *et al* do not pertain to anhydrous 1Zn:2Cl compounds but to $ZnCl_2$ crystals stabilized by water and/or oxide. It is also surprising that the calculations performed for the hypothetical water/oxide free α-, β- and γ-$ZnCl_2$ crystals match so well the experimental data corresponding to $ZnCl_2$ compounds highly contaminated by water and/or oxide.

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