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THE TETRAFLUOROALUMINATES $AAlF_4$ (A = Tl, K, Rb): A SMALL FAMILY WITH VARIOUS STRUCTURAL PHASE TRANSITIONS

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Investigations of the tetrafluoroaluminates temperature behaviour have been undertaken in order to find and to study structural phase transitions (SPT) in layered materials in connection with lattice dynamics analysis. The tetrafluoroaluminates, which consist of AlF_6 octahedra sheets **(1)** have been chosen for their diamagnetic character, their high symmetry and their structure closely related to the well known (fluoro) perovskite structure whose behaviour has been accurately studied. Moreover it has been shown that the SPT are generally related to a freezing of some low frequency phonon in the Brillouin zone so that the mechanism of the transitions can be often explained from a phonon spectrum study. In case of fluorides, owing to the small polarizability and the high ionicity of fluorine ions the phonon spectrum can be calculated using a rigid ion model which involves a small number of parameters (short range interaction between two nearest neighbour ions and effective ionic charges).

$RbAlF_4$, $KAlF_4$ and $TlAlF_4$ were studied. In $RbAlF_4$ two SPT have been observed at T_1 = 280° C and at T_2 = 9° C. The structure analysis shows that $RbAlF_4$ has the aristotype structure above T_1 (phase I_{Rb}) ; between T_1 and T_2 (phase II_{Rb}) the AlF_6 octahedra are tilted around the [001] axis and below T_2 (phase III_{Rb}) additional tilts around [100] and [010] axes appear **(2)**. $TlAlF_4$ also undergoes two SPT at T_1 = 241 °C and at T_2 = 162° C **(3)**. Though the aristotype structure is called '$TlAlF_4$ structure' this structure exists only above T_1 (phase I_{Tl}). On the other hand $KAlF_4$ undergoes only one SPT **(4)** at T = - 13° C. It never has the aristotype structure : its room temperature structure is similar to $RbAlF_4$-phase II_{Rb}. The SPT is reconstructive and comes from gliding of AlF_6 octahedra sheets. It leads to a $KFeF_4$ type structure. This shear transformation, typical of the layered structure is very similar to the so-called martensitic transformation in metallic alloys.

The rigid ion model to calculate the phonon spectrum has been first adjusted for $RbAlF_4$ **(5)**. The difference with experimental data (obtained from ultrasons, Raman scattering, infrared absorption and inelastic neutron scattering) is less than 10 %. In extending the results to $KAlF_4$ we have determined the characteristics of the phonons responsible for the transition and we deduce the mechanism inducing the AlF_6 octahedra sheets gliding

(5). In applying the model to $TlAlF_4$ we have predicted the phonons whose freezing could induce SPT and the possible space groups for the successive phases **(3).**

So the knowledge of the phonon spectrum, whenever it is possible, is a convenient tool to explain the mechanism of the SPT and may even be useful in the search for struc consecutive to a phase transition. The present model can be applied to any AMF_4 material where other kinds of transitions are observed.

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