

07.3-7 VARIOUS TYPES OF IONIC CONDUCTIVITY IN RbNbWO_6 AND TlNbWO_6 RESULTING FROM STRUCTURE.

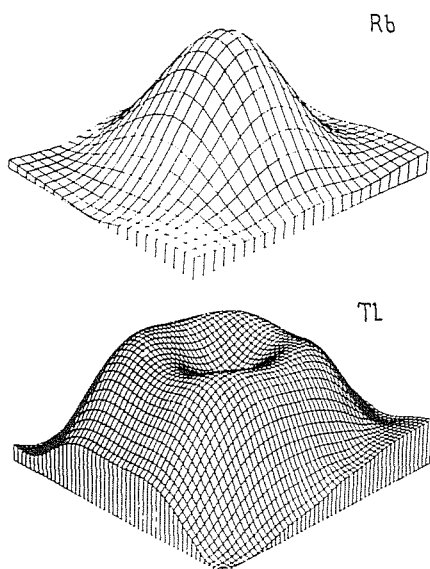
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Ferroelectric-superionic phase transition is known to be observed in RbNbWO_6 and TlNbWO_6 crystals at T 330 K and T 360 K, respectively. Precise neutron-structure investigation of monocrystals at T 423 K and T 573 K has been carried out.

The structures consist of a three-dimensional framework similar to that of pyrochlore with Rb and Tl ions being positioned in large octahedral vacancies. Framework geometry of the two compounds is very much the same, but the positions of Rb and Tl ions in equidimensional octahedrons are significantly different. As is seen from the Figures, a Rb cation is localized in the centre of the octahedron, while a Tl cation is displaced by 0.6 Å to the centres of the octahedron planes. Statistically the latter occupies eight sites which are covered by two crystallographically independent positions in the $Fd\bar{3}m$ Fedorov symmetry group. The situation is not ordinary for classic crystal chemistry of inorganic compounds.

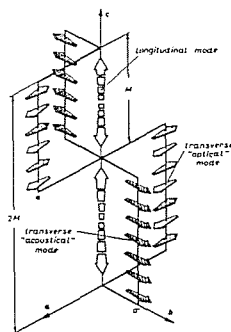
Noticeable deviation of Rb ion heat oscillations from the harmonic law has been observed at T 573 K. Difference chart for the probability of the Rb cation distribution obtained by the elimination of a harmonic component, is in favour of the Rb ion displacement towards the windows edging the octahedral sites. Corresponding interactions in this chart are similar to the charts of the statistical Tl ion position TlNbWO_6 .

Traces of cation diffusion in the process of the ionic transportation in the structures under study are similar. Difference of conductivity in the compounds is due to the position of Rb and Tl ions in the structure.



07.4-1 GENERALIZED WIGNER CRYSTAL IN QUASI 1-D PLATINUM CHAIN COMPOUNDS. by A. Bertinotti, D. Luzet, Service de Physique du Solide et de Résonance Magnétique CEN-Saclay 91191 Gif-sur-Yvette Cedex, France

Since the original observations on partially oxidized tetracyanoplatinates (KCP), the columnar structures of mixed-valence platinum chain compounds have been considered the typical example of charge density wave states in quasi 1-dimensional systems. Detailed structural results derived successively from the temperature dependent satellite spectra observed in bis(oxalato) platinate salts have led however to a new interpretation based on the generalized Wigner crystal concept (A. Bertinotti, D. Luzet, Europhys. Lett., 1 (4) pp.181-187 (1985). There is no more in these structures a continuous modulation of the conduction electron density but a fragmentation into periodic domains locally commensurate with the underlying lattice, but "statistically" incommensurate, leading to a quasi-lattice for the electrons. Description will be given of the relatively complex pattern of inter- and intra-columnar dispersive modes affecting the structure and of the periodic antiphase ordering of the counter-ions which have been brought to light (fig.1). Together with the quantitative verification of the new type of order its adequacy for explaining the observations concerning the structural transformations and their symmetry relationships, the microscopic aspect of the metal insulator transition, and the long range coherence between electrons and counter-ions will be presented.

07.4-2 THE TETRABUTYLAMMONIUM SALT OF DIMERIZED BIS(DISELENOLATOISOTRITHIONE) NICKEL (III), $(\text{TBA})_2[\text{Ni}(\text{dsit})_2]_2$. By Bruno Morosin and Paul J. Nigrey. Sandia National Laboratories, Albuquerque, NM 87185 USA.

A new class of organic metals employs as one of the starting reagents bis(tetrabutylammonium) bis(diselenolatoisotrithione)nickelate(II), $(\text{TBA})_2[\text{Ni}(\text{dsit})_2]$. The essentially flat $\text{Ni}(\text{dsit})_2$ anions may contain nickel in the +2 and +3 formal oxidation state, similar to that observed in the all sulfur nickel chelate, $\text{Ni}(\text{dmit})_2$ [1]. The tetrathiafulvalene, TTF, charge-transfer salt of $\text{Ni}(\text{dmit})_2$ has interesting low temperature metallic behavior. Attempts to prepare $(\text{TTF})[\text{Ni}(\text{dsit})_2]_2$ by diffusion growth, resulted in black plates of the above titled dimer.

$(\text{TBA})_2[\text{Ni}(\text{dsit})_2]_2$ crystallizes in $P\bar{1}$ with $a = 12.409$, $b = 14.044$, $c = 9.601\text{Å}$, $\alpha = 94.42$, $\beta = 80.23$, $\gamma = 98.64^\circ$ with $Z = 1$. The $\text{Ni}(\text{dsit})_2$ dimers require some distortion of the normally flat monomer units [2] which is best seen in comparison of Se-Ni-Se angles (the 180° monomer values are 153 and 176 in the dimer). The nickel environment consists of a square pyramid (four 2.33Å plus an apex 2.49Å Ni-Se bonds) with nickel displaced above the square base; two such pyramids share an edge in the dimer resulting in a 3.35Å Ni-Ni interaction. The other bond separations are similar to those observed in the monomer nickel chelates [1,2].

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[1] O. Lindquest, et al., Acta Chem. Scand. **A33** 445(1979)

[2] B. Morosin and P. J. Nigrey, ACA Austin Meeting, Mar 1987