07. MATERIALS SCIENCE

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 tetracyanonplatinates (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)platinates 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 intra- and inter-columnar displative 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.

07.3.7 VARIOUS TYPES OF IONIC CONDUCTIVITY IN RbNbW0 6 AND TlNbW0 6 RESULTING FROM STRUCTURAL


Perovskite-superionic phase transition is known to be observed in RbNbW0 6 and TlNbW0 6 crystals at T 330 K and T 360 K, respectively. Precise neutron-structure investigation of monoclinic crystals at T 343 K and T 573 K has been carried out.

The structures consist of a three-dimensional framework similar to that of pyrochlore with a Rb and Tl ions being positioned in large octahedral vacancies. Framework geometry of the TlNbW0 6 material shows a close resemblance to that of pyrochlore with Rb and Tl ions in equidimensional positions, but the two compounds are 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 towards the centres of the octahedron planes. Statistically the latter occupies eight sites which are covered by two crystallographically independent positions in the P63mc 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 (fig.3). 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. Traces of cation diffusion in the process of the ionic transportation in the structures under study are similar. Difference of conductivity in the compounds to the position of Rb and Tl ions in the structure.