

**05.X-03** HIGH PRESSURE INDUCED COMMENSURABILITY EFFECTS ON THE PEIERLS TRANSITIONS IN AN ORGANIC METAL : TTF-TCNQ

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TTF-TCNQ has been shown earlier to undergo several successive Fermi surface driven Peierls transitions. This is due to the fact that this compound is built of segregated stacks of TTF and TCNQ molecules which constitute two slightly different one dimensional metallic chains. Two different kind of commensurability effects are observed in this compound.

Temperature and pressure first modify the coupling between the two sets of chains, leading in the low temperature insulating phases to variable transverse components of the modulation in  $\tilde{a}$  direction, with successive locking at the commensurable values  $4a$ ,  $2a$ ,  $1a$ .

Temperature and pressure, but mostly pressure, secondly change the overlap of the  $\pi$  molecular orbitals along the stacks which are responsible for the metallic properties ; therefore the charge transfer between the donor TTF and acceptor TCNQ molecules which determines the value of the Fermi wave vector  $k_F$  is modified. Consequently the longitudinal modulation period ( $= b \times 2\pi/2k_F$ ) varies. One observes indeed that the Fermi wave vector which is incommensurable at ambient pressure ( $2k_F = 0.295 b^*$ ), increases under applied pressure until it locks at the commensurable value of  $2k_F = 1/3 b^*$  observed at 14.5 and 17 Kbars.

A particular interest of such commensurability effects is that they are, in such systems, directly related to modifications of the transport properties.

**05.1-01** TRANSITIONS BETWEEN PHASES WHICH HAVE NO GROUP-SUBGROUP RELATIONSHIP. By P. Toledano, Groupe de Physique théorique, UER de Sciences, 33 rue Saint-Leu, 80039 Amiens Cedex, France.

In several substances, among which figures a large fraction of the elements, there are transitions which are not group-subgroup related. For these substances the question is stated whether some general properties can be derived from the corresponding structural change or if their phenomenological features are unpredictable. We examine the various situations which may be encountered on that score. Two main classes of transitions are distinguished owing to an essential difference in their microscopical mechanism : 1) A first class contains the transitions for which the rearrangement of structure is such that no rupture of the atomic bonds occurs, but only displacements of atoms from one equilibrium site to another. In this case it is shown that the space groups  $G_1$  and  $G_2$  of the two phases possess either a common parent group or a common subgroup. In both cases a phenomenological description can be performed providing one or several order-parameters. A number of illustrative examples are discussed among which carbon bromide, lithium iodide and the  $M_3M^{III}(XO_4)_2$  family (B. Jolibois et al, Acta. Cryst. (1980) B36, 2517). 2) A second class contains substances for which the structure of one phase is broken down and reconstructed in a new one forming a modified packing of the atoms with a partial rupture of the atomic bonds. In this case it is shown that two sorts of parameters have to be used for a phenomenological description. A first set, composed by order-parameters of the Landau-type describes the phase-change associated to the preserved portion of the system. An additional set of parameters expresses the loss of informations corresponding to the restructuring part of the lattice and indicates the disruptions undergone by the system. Examples of such parameters are given for experimentally observed martensitic transformations and for transitions taking place within the elements.

**05.1-02** A VARIATIONAL APPROACH TO SHORT-RANGE ORDER INTENSITY. By J. M. Sanchez and D. de Fontaine, Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720, USA.

A staggered field method is proposed for calculating the short-range order (SRO) intensity in binary alloys (Ising systems, in general) using the functions generated by the cluster variation method (CVM) as approximate free energy expressions. The method is exact. When the CVM free energy function is also exact, as in the one-dimensional Ising model, the integrated SRO intensity remains strictly constant at all temperatures. For higher-dimensional cases, the calculated integrated intensity can be used as a sensitive measure of the level of approximation, the CVM performing well at high temperature and breaking down, as expected, near critical points. The calculated SRO intensity reduces to the well-known Krivoglaž-Clapp-Moss formula when the free energy is written in the Bragg-Williams approximation. Higher CVM approximations are seen to behave much better in terms of the constancy of integrated SRO. The new CVM-derived SRO intensity is also consistent with the CVM derivation of corresponding phase diagrams. Theoretical calculations will be compared to experimental SRO intensity data for the Cu-Au system.

**05.1-03** THE USE OF GROUP THEORY FOR CALCULATING THE CONFIGURATIONAL ENTROPY IN THE CLUSTER VARIATION APPROXIMATION. By D. Gratias<sup>†</sup>, J. M. Sanchez and D. de Fontaine, Department of Materials Science & Mineral Engineering, University of California, Berkeley, CA 94720, USA. (<sup>†</sup> Permanent address: C.E.C.M./CNRS, 15 rue G. Urbain, 94400-Vitry, FRANCE)

One of the difficulties encountered in the Cluster Variation Method (CVM) is that of calculating approximate expressions for the number  $\Omega$  of configurations of a crystal lattice having specified distributions of clusters (pairs, triads, ...). The methods proposed up to now are based on the knowledge of the number of equivalent subclusters contained in a given basic cluster. A simple way of determining these numbers is proposed for any type of cluster in a general structure based on group theory considerations: given two clusters  $A$  and  $A'$  ( $A'$  being a subcluster of  $A$ ) and their normalizer  $N_A$  and  $N_{A'}$  in the symmetry group  $G$  of the crystal, let  $N_{AA'}$  be their intersection group; then the index of  $N_{AA'}$  in  $N_A$  represents the number of  $A'$  equivalent clusters contained in  $A$ , while the index of  $N_{AA'}$  in  $N_{A'}$  represents the number of  $A$  equivalent clusters containing  $A'$ . The determination of these indices for all clusters involved in the chosen approximation leads directly to the entropy expression. Moreover, a general expression for  $\Omega$  can be given, which leads to an iterative formula relating any two successive orders of approximation.