

CRYSTALLINE PHASE TRANSITIONS OF $K_3Lu(PO_4)_2$. AN ELECTRON PARAMAGNETIC RESONANCE PECULIAR VIEWJ.L. Boldu¹ L.A. Boatner² E. Mu@oz¹ J. Barreto¹ J.M. Farmer²¹Instituto De Fisica, UNAM Estado Solido Circuito De La Investigacion Cientifica S/N Ciudad Universitaria MEXICO CITY D.F. 01000 MEXICO²Oak Ridge National Laboratory

An electron paramagnetic resonance (EPR) study is performed on $K_3Lu(PO_4)_2$ using trivalent gadolinium ions as a paramagnetic probe. At room temperature, Gd^{3+} was found to replace a Lu constituent ion thereby exhibiting, a hexagonal crystal field configuration ($P-3$) that preserves the six-fold coordination. Upon cooling the sample, a phase transition occurs at 242 K in agreement with the heat capacity measurements*, and the EPR spectrum suddenly transforms into a more complex crystalline structure ($P2_1/m$). Around 153 K, progressive changes in the spectrum signal the onset of a second phase transition that continues down to 113 K. Then, irreversible cracks at the sample, presumably due to the fatal change in coordination number, prevent further studies to complete the possible hysteresis cycle.

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DIFFUSE PHENOMENA IN CO-CRYSTALS DISPLAYING MORPHODICHOTOMY AND SEGREGABILITY

M. Bonin M. Hostettler G. Chapuis K. Schenk

Institute of Crystallography University of Lausanne LAUSANNE 1015 SWITZERLAND

The morphological dichotomy of urotropin U (ball) and azelaic acid (stick) gives rise to co-crystals characterized by solvent inclusions, high vacancy and dislocation densities. These defects, with the tendency of U to leave the crystal, leads to rather special phase transitions, incommensurate phases and a peritectoid reaction in the recrystallization regime. The ambient phase can be described as an OD structure [M. Bonin et al., to be submitted]. This OD character exists between 10 and 96° C, but there are no less than five distinct phases that appear as bumps in calorimetry. They present different OD or incommensurate structures. The corresponding transitions are accompanied by solvent extrusion, recrystallization of U in wrinkles on the surface and fast moving phase fronts. Above 80° C the loss of U becomes important leading to a competition between a 3D crystal and a liquid-crystal type [M. Gardon et al., to be published in Phys. Rev. Lett.]. At low temperature, two transitions take place. First, a triggered improper ferroelastic transition [M. Hostettler et al., Acta Cryst. B55, 1999], then a destructive one leading to an ordered structure via slip systems activated by releasing internally stored energy (this may explain why such a destructive process exhibits a small transition enthalpy). The diffuse scattering is modelled by Monte-Carlo simulations involving occupational variables and chain shifts. These random shifts are thought to trigger the incommensurate phases. The analysis of the observed diffuse intensities explains the structural changes between 65 and 10° C.

Keywords: DIFFUSE SCATTERING SIMULATION DEFECTS

PREDICTION OF NEW FERROELECTRICS WITH SYMMETRY $Pna2_1$

C. Capillas E. Kroumova M.I. Aroyo J. M. Perez-Mato

Universidad Del Pais Vasco Fisica De La Materia Condensada Apdo 644 BILBAO VIZCAYA 48080 SPAIN

A compound may be considered as possible ferroelectric if a small distortion of the structure can lead to change of its symmetry from polar to non-polar one. If this distortion is small enough the structure is pseudosymmetric with respect to the higher non-polar symmetry. Therefore the prediction of new ferroelectric materials can be based on a search for pseudosymmetric structures among that having polar symmetry. This structural criterium has been used with success[1] since 1971 for the prediction of new ferroelectric materials. We have developed a procedure for systematic search for pseudosymmetry among a set of compounds[2] and generalized it for the ferroelectric case[3]. The PSEUDO program provides a web tool for performing this systematic search and it forms part of the "Bilbao Crystallographic Server" (www.cryst.ehu.es). The search of new ferroelectrics has been applied on the binary, ternary and quaternary compounds with symmetry $Pna2_1$ listed in the Inorganic Crystal Structure Database[4]. In addition our results are compared with those obtained by electron density method for pseudosymmetry search[5].

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CRYSTAL STRUCTURES OF CYANO-ELPASOLITES: CHEMICAL PRESSURE VERSUS TEMPERATURE

D. Chernyshov H.-B. Bürgi

Bern University Bern University Laboratorium For Chem. Und Mineral. Crystallography Freiestr. 3 BERN CH-3012 SWITZERLAND

The room temperature structures of the cyano-elpasolites $A_2BM(CN)_6$ ($A=Cs, Rb; B=Li, Na, K, Rb; M=Cr, Mn, Fe, Co$) available in the literature have been analyzed as a function of the cavity size available for the A-cation in the undistorted, cubic high-temperature modification. The crystal structure of $Cs_2NaCo(CN)_6$ has been studied by X-ray diffraction as a function of temperature ($T=100-635$ K). The two series of data show astonishing similarities. If the cavity for A is small or T is large, both series of data show the cubic $Fm\bar{3}m$ phase. With increasing cavity size or decreasing temperature, a first order structural phase transition (SPT) to a $P4/mnc$ phase takes place, followed by a 2nd order SPT to a monoclinic $P2_1/n$ phase. In the first transition the $M(CN)_6$ groups rotate about an MCN vector and produce a layered tetragonal structure. In both series of data the second SPT involves two order parameters and is realized in two stages. First, the A-cations are displaced within the layers and, second, the $M(CN)_6$ octahedra are further rotated about an axis in the layer and between two CN groups. The two order parameters show different critical behavior. For very large cavities an additional out-of-layer displacement of the A-cation is observed, consistent with a Gamma-point phonon $B1g$ in $P4/mnc$ and indicating the possibility of an additional SPT. Such a transition has not yet been observed in temperature dependent experiments.

Keywords: STRUCTURE PHASE TRANSITIONS, CYANO-ELPASOLITES, CRITICAL BEHAVIOR