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Antiferroelectric phase transition in titanite: Excess entropy and short range order

STUART A. HAYWARD,[1,*] JAIME DEL CERRO,[1] AND EKHARD K.H. SALJE[2]

[1]Departamento de Fisica de la Materia Condensada, Universidad de Sevilla, P.O. Box 1065, E-41080 Sevilla, Spain
[2]Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.

ABSTRACT

The antiferroelectric $A2/a \leftrightarrow P2_1/a$ phase transition in titanite may be described using a thermodynamic model where the principal contribution to the excess entropy is assumed to be configurational rather than vibrational; $G = \mathrm{A}/2\ Q^2 + B/4\ Q^4 + \lambda T\,[(1 + Q)\ln(1 + Q) + (1 - Q)\ln(1 - Q)]$. Such a model is likely to be a valid description of a phase transition where strain effects are large enough to maintain mean field behavior, but not so large that vibrational effects dominate in the excess entropy. Best-fit parameters for A/λ and B/λ are determined from X-ray measurements of the order parameter. The magnitudes of the three parameters are then determined using calorimetric data, with the results $A = -337.6$ J/mol, $B = -112.5$ J/mol, $\lambda = 0.34$ J/mol-K. The model is compared with measurements of dielectric susceptibility, and is found to give good, but not perfect, agreement with experiment. The excess entropy associated with the transition is far smaller than expected for a simple order-disorder model. This is interpreted as evidence for significant short-range order above T_C.