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

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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; \(G = A/2 Q^2 + B/4 Q^4 + \lambda T \ [\ln (1 + Q) + (1 – Q) \ln (1 – Q)]\). 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 \(A/\lambda\) and \(B/\lambda\) 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 \(\lambda = -337.6 \text{ J/mol}, \ \Lambda = -112.5 \text{ J/mol}, \ \beta = 0.34 \text{ J/mol-K}\). 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 \(T_c\).

INTRODUCTION

The crystal structure of titanite consists of a framework of \(\text{TiO}_6\) octahedra and \(\text{SiO}_4\) tetrahedra. Octahedra share corners to form chains, which run parallel to the crystallographic \(c\)-axis, with chains linked by the silicate tetrahedra. Ca cations sit in the resulting large cavities in the framework, in irregular sevenfold-coordinated sites (e.g., Taylor and Brown 1976).

As might be expected, titanite has several distinct phase transitions, involving several of the potential instabilities in this crystal structure (Chrosch et al. 1997). This study is concerned with the phase transition at approximately 500 K associated with the off centering of Ti cations within their octahedra. In this transition, the macroscopic space group symmetry is reduced from \(A2/a\) to \(P2_1/a\). This symmetry change is consistent with an antiferroelectric transition, with linked chains of octahedra developing equal and opposite dipoles.

The antiferroelectric phase transition has several intriguing features, the connections between which are not entirely clear. The most striking factor to emerge from the studies of the temperature dependence of the order parameter (e.g., Ghose et al. 1991; Bismayer et al. 1992; Zhang et al. 1995; Chrosch et al. 1997) is the extremely low value of \(\beta\) obtained when the available data is fitted to a power law, \(Q \propto |T_c – T|^\beta\). Typically, values around 0.14 are observed. An obvious contrast can be drawn with the predictions of the Landau theory of phase transitions, which predicts that \(\beta\) is in the range 0.25 (at the tricritical point) to 0.5 (in the second order limit).

Another common factor in many studies is the presence and behavior of thick mobile antiphase boundaries (e.g., Speer and Gibbs 1976; Van Heurck et al. 1991; Chrosch et al. 1997). These appear to be related to the presence of impurities, particularly on the Ti sites, and have the effect of “smearing” the transition; natural samples with a high enough concentration of impurities and many APBs do not display evidence for a phase transition at all.

The final significant factor is the evidence for short-range order persisting above the transition temperature. Bismayer et al. (1992) noted the persistence of superlattice diffraction maxima above \(T_c\). This feature was investigated more fully by Chrosch et al. (1997), who measured the profile of this diffuse scattering below and above \(T_c\). Below the transition temperature, the main diffuse signal had a width corresponding to a real space length scale of ca. 500 Å. Above the transition temperature, the diffuse scattering became broader, corresponding to a reduction in the length scale of the real space correlations being observed.

Further progress requires a better understanding of the thermodynamics of this phase transition. We can ask what type of model is consistent with the small apparent critical exponent observed in this transition. This model may also provide insights as to the extent to which short-range order does modify the transition behavior.

In this study, a model of the 500 K phase transition in titanite is developed, similar to that used by Kroll et al. (1994) to describe (Fe, Mg) ordering in orthopyroxenes. The model may be regarded as an intermediate case between the Bragg-Williams and Landau models of phase transitions. Similar to the Landau potential, most interactions are only considered to the extent that their symmetry constrains the way that their contribution to the overall energy varies with the order parameter \(Q\).