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Structural model of order–order transition state in titanium monoxide $TiO_{1.0}$

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Calculation of configurational entropy of the order–order transition structure

The configuration entropy S appearing as a result of certain disorder in the distribution of vacancies in transition structure at the order parameters $\eta_{cub} \neq 0.2667$ and $\eta_{cub} \neq 1$ can be found by the Boltzmann formula

$$S = k_B \ln \Omega \,, \tag{1}$$

where Ω is the number of microstates of a system, with the help of which a given macrostate is realized, and k_B is the Boltzmann constant. The value of Ω is determined for a group of sites by a combinatorial formula

$$\Omega = \frac{M!}{K!(M-K)!} \,,$$

where M is the number of sites in the considered group and K is the number of sites in the given sublattice that are occupied by atoms or vacancies. In the assumed model (*AB* path in fig. 1), disorder is possible only in purely monoclinic or purely cubic vacancy positions. The calculation of the $S(\eta_{cub})$ dependence should be carried out separately for two groups of positions, and the entropy of a crystal is determined as a sum of entropies of the considered groups:

$$S_{tot} = S_{mon} + S_{cub} \,. \tag{2}$$

The factorial logarithms were taken using the Stirling formula

$$\ln N! \approx N \ln N - N \,.$$

Then, considering the logarithm properties, expression (1) is transformed into

$$S = k_B(M \ln M - K \ln K - (M - K)\ln(M - K)), \tag{3}$$

and thereby the problem comes to finding the values of *M* and *K*.

If the processes of ordering in titanium and oxygen sublattices are similar, then *M* and *K* can be calculated summarily for metal and oxygen vacancy positions. If there are *N* *B*1 structure sites in the crystal, then, according to the peculiarities of M_5X_5 superstructures, 1/6*N* sites are vacancy sites, 38.89 % of which in the assumed model give no contribution to the configuration entropy. Therefore, *M* is

$$M = \frac{1}{6} \cdot 0.6111 N . \tag{4}$$

K, as distinct from *M*, depends on the order parameter. The fraction of atoms in the vacancy sublattice of M_5X_5 type superstructure is 5/6–5/6η. Since 38.89 % of sites are always vacant, the quantity of atoms contributing to entropy will be 1/0.6111 times larger. As a result, we have

$$K = M\left(\frac{5}{6} - \frac{5}{6}\eta\right)/0.6111 . \tag{5}$$

For convenience, we introduce the value $K' = K/M$ instead of *K* and $M' = M/N$ instead of *M*. In view of (4) and (5), expression (3) is transformed into

$$S = k_B NM'(\ln M' - K' \ln M'K' - (1 - K')\ln(M' - M'K')) . \tag{6}$$

Using (6) for both S_{mon} and S_{cub} the total entropy can be found according to (2).