

Temperature Dependent Re L₃-Edge X-Ray Absorption Study of Crystalline Rhenium Trioxide ReO₃

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Abstract. X-ray absorption spectroscopy study of crystalline ReO₃ was performed at the Re L₃-edge in the temperature interval from 77 to 670 K. The analysis of both XANES and EXAFS regions shows that in ReO₃, a progressive localization of the 5d states following the temperature increase is accompanied at $T > 350$ K by a distortion of the ReO₆ octahedra. The distortion increases continuously up to the ReO₃ decomposition temperature $T_d \approx 673$ K and leads to the lowering of the rhenium site symmetry from O_h ($T \leq 350$ K) $\rightarrow D_{4h}$ ($T \approx 513$ K) $\rightarrow C_{4v}$ ($T \approx 668$ K). The observed distortion is explained by (i) the strong electron-phonon coupling of the 5d electron with the M_3 and $M_3'^2$ phonons and (ii) the Jahn-Teller-like effect caused by the rhenium 5d¹ electron which becomes localized at high temperature.

X-ray absorption spectroscopy study of polycrystalline rhenium trioxide ReO₃ has been performed on the Re L₃-edge in the temperature range from 77 K up to the ReO₃ decomposition point $T_d \approx 673$ K. The x-ray absorption spectra were measured in transmission mode at the ADONE (Frascati) and DCI (Orsay) storage rings, and the experimental details can be found in [1]. ReO₃ has a perovskite-type cubic structure composed of regular ReO₆ octahedra joined by vertices. Rhenium ions Re⁶⁺ in ReO₃ have 5d¹ electronic configuration resulting in the partially filled 5d-band and metallic conductivity [2]. The presence of 5d-electron is responsible for the stability of the ReO₃ lattice and the absence of any structural phase transitions at atmospheric pressure that is opposite to many other perovskites (BaTiO₃, SrTiO₃ etc) and perovskite-like compounds (WO₃).

The XANES analysis shows that a strong modification of the local electronic structure occurs with increasing temperature. It can be explained (1) by a progressive narrowing of the t_{2g} and e_g sub-bands with a localization of the electron states (especially having e_g character) at rhenium sites due to the electron-phonon coupling (Figure 1(a)) and (2) by an increase at $T > 470$ K of the effective charge on rhenium ions leading to a shift in the position of the absorption edge and the white line (WL) maximum (Figure 1(b)).

The analysis of EXAFS suggests that a distortion of the ReO₆ octahedra occurs at $T \approx 380$ K while the sub-lattice formed by Re atoms remains regular. This conclusion is supported by the dependence of the average mean square relative displacements (MSRD) $\sigma^2 (= \sigma_{th}^2 + \sigma_{st}^2)$ on the temperature (Figure 2). The deviation of the MSRD $\sigma^2(\text{Re-O}_1)$ in the 1st shell from the Debye model behaviour means that for $T > 350$ K, both thermal σ_{th}^2 and static σ_{st}^2 disorder are present (Figure 2(a)). At the same time, the MSRD $\sigma^2(\text{Re-Re}_4)$ in the 4th shell follows the Debye law (Figure 2(b)) so that the static distortion of the rhenium sub-lattice is expected only near the decomposition temperature T_d (see the last point in Figure 2(b)). The results of the MSRD analysis agree well with the radial distribution functions (RDF) obtained for the 1st shell of rhenium (Figure 3(a)). Thus, we suggest the following model for the modifications occurring within the ReO₃ structure upon heating. The electron-phonon coupling, caused by the M_3 phonon mode, leads already at low-temperatures to the progressive localization of the 5d states at rhenium sites. This process results at $T > 350$ K in the localization of the 5d¹ electron and the Jahn-Teller-like distortion (Figure 3(a)) leading to the lowering of the local symmetry at rhenium sites from O_h to D_{4h} . On temperature increase, at $T \approx 563$ K, the further distortion of the ReO₆ octahedra from D_{4h} to C_{4v} local symmetry appears which can be explained by the coupling of the 5d electron with the $M_3'^2$ phonons.

The obtained results suggest that the stability of the ReO₃ lattice, caused by the presence of the 5d¹-electron, can be broken by temperature increase and, thus, the temperature dependence of the ReO₃ conductivity at high temperatures ($500 < T < 670$ K) could deviate from its low-temperature behaviour.

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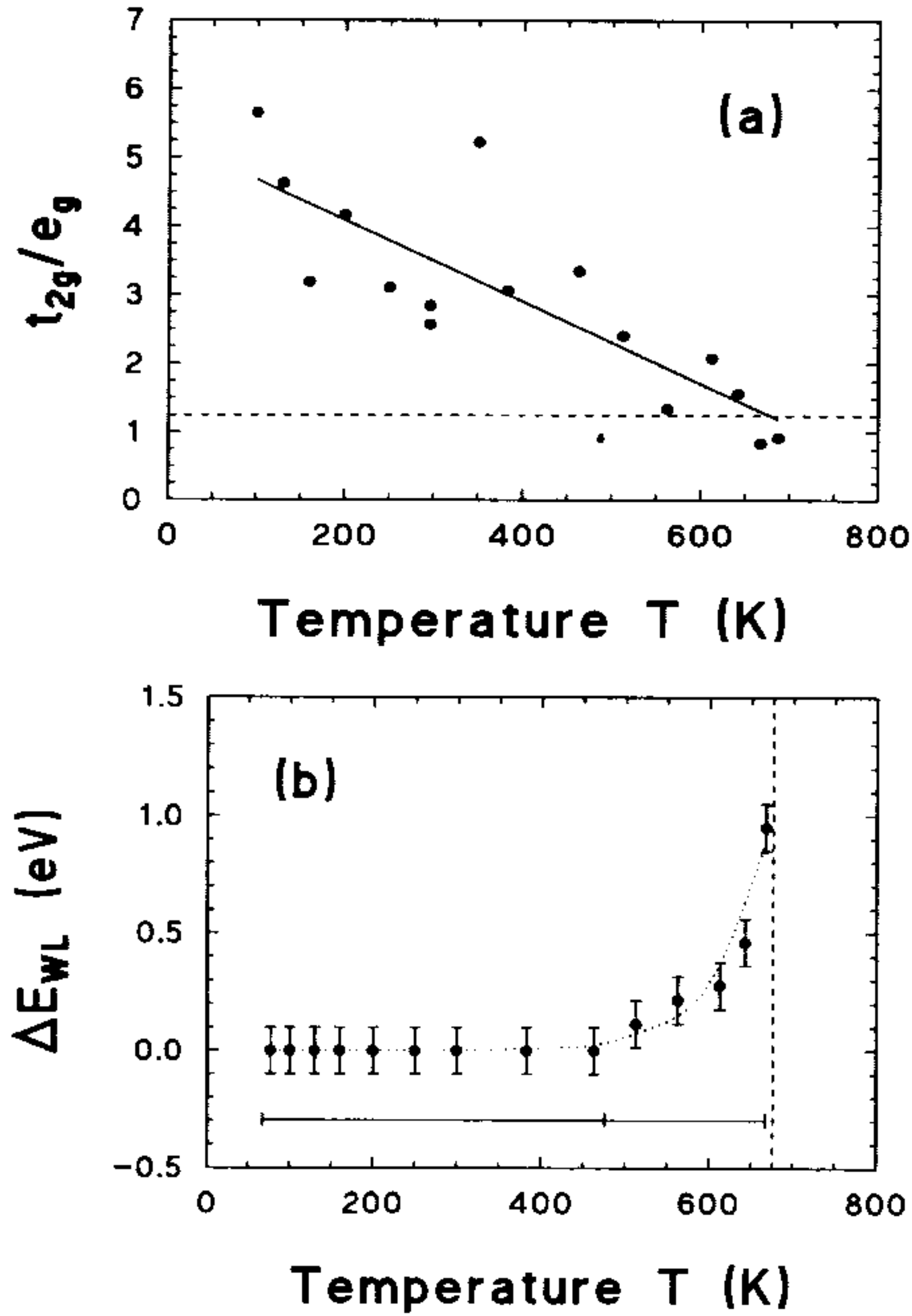


Figure 1: (a) Temperature dependence of the ratio t_{2g}/e_g :

$$t_{2g}/e_g = \frac{\langle t_{2g}(\pi) | \hat{\epsilon} \cdot \vec{r} | 2p_{3/2} \rangle^2 N(t_{2g}(\pi), E)}{\langle e_g(\sigma) | \hat{\epsilon} \cdot \vec{r} | 2p_{3/2} \rangle^2 N(e_g(\sigma), E)}$$

which shows the variation of the number of the free states and the localization degree for two sub-bands. The dashed line corresponds to the fully localized orbitals with the number of unoccupied states equal to five in t_{2g} and four in e_g sub-bands. (b) Temperature dependence of the WL maximum shift ΔE . Dotted line is a guide for eye. Vertical dashed line shows the ReO_3 decomposition temperature $T_d \approx 673$ K.

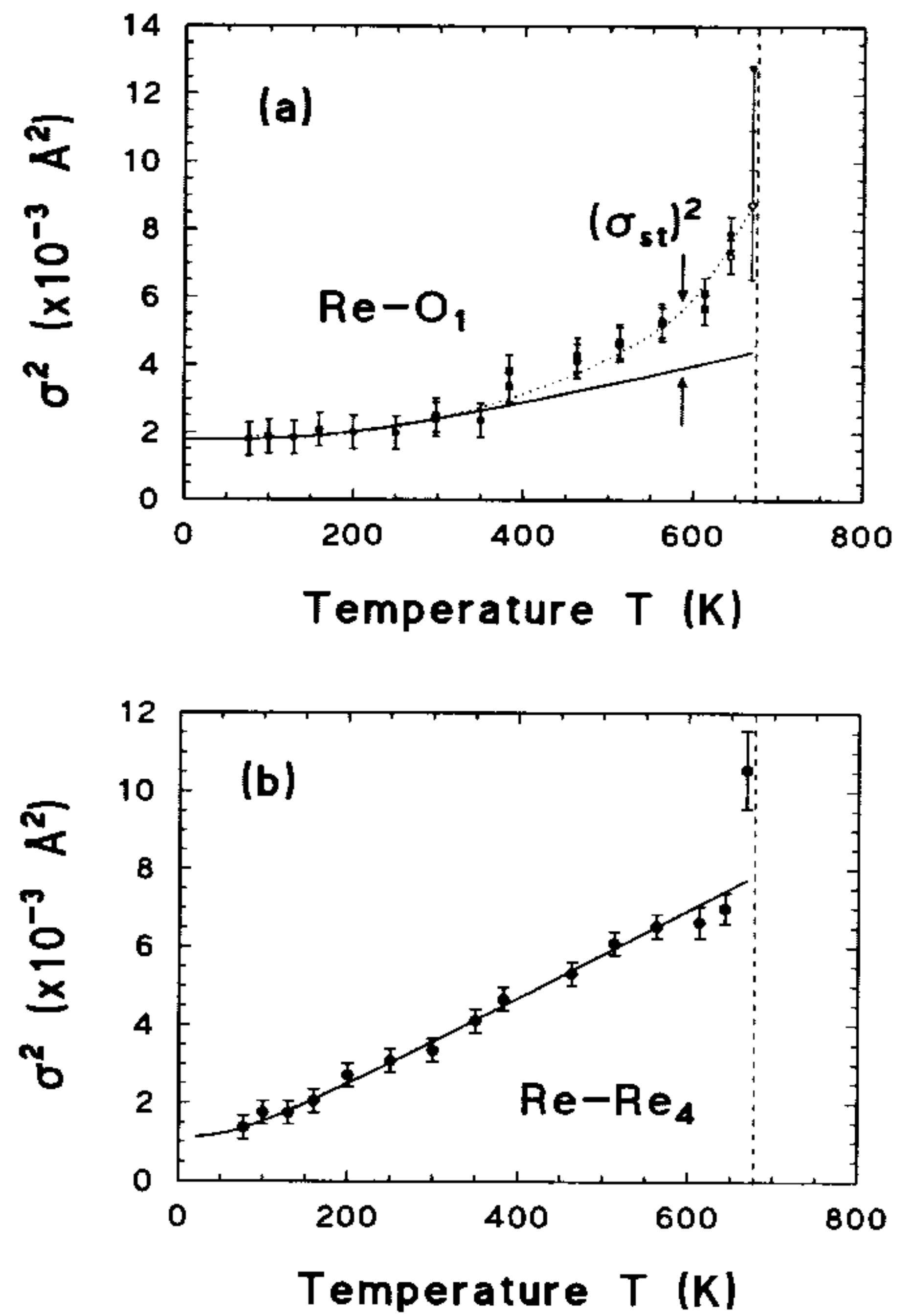


Figure 2: (a) Temperature dependence of the average MSD σ^2 in the first shell of rhenium. Solid line correspond to the MSD given by the Debye model with $\Theta_D = 780$ K. Dotted line is a guide for eye. (b) Temperature dependence of the MSD for the Re-Re_4 ($R \approx 5.3$ Å) atom pair. Solid line corresponds to the correlated Debye model with $\Theta_D = 333$ K. Vertical dashed line shows the ReO_3 decomposition temperature $T_d \approx 673$ K.

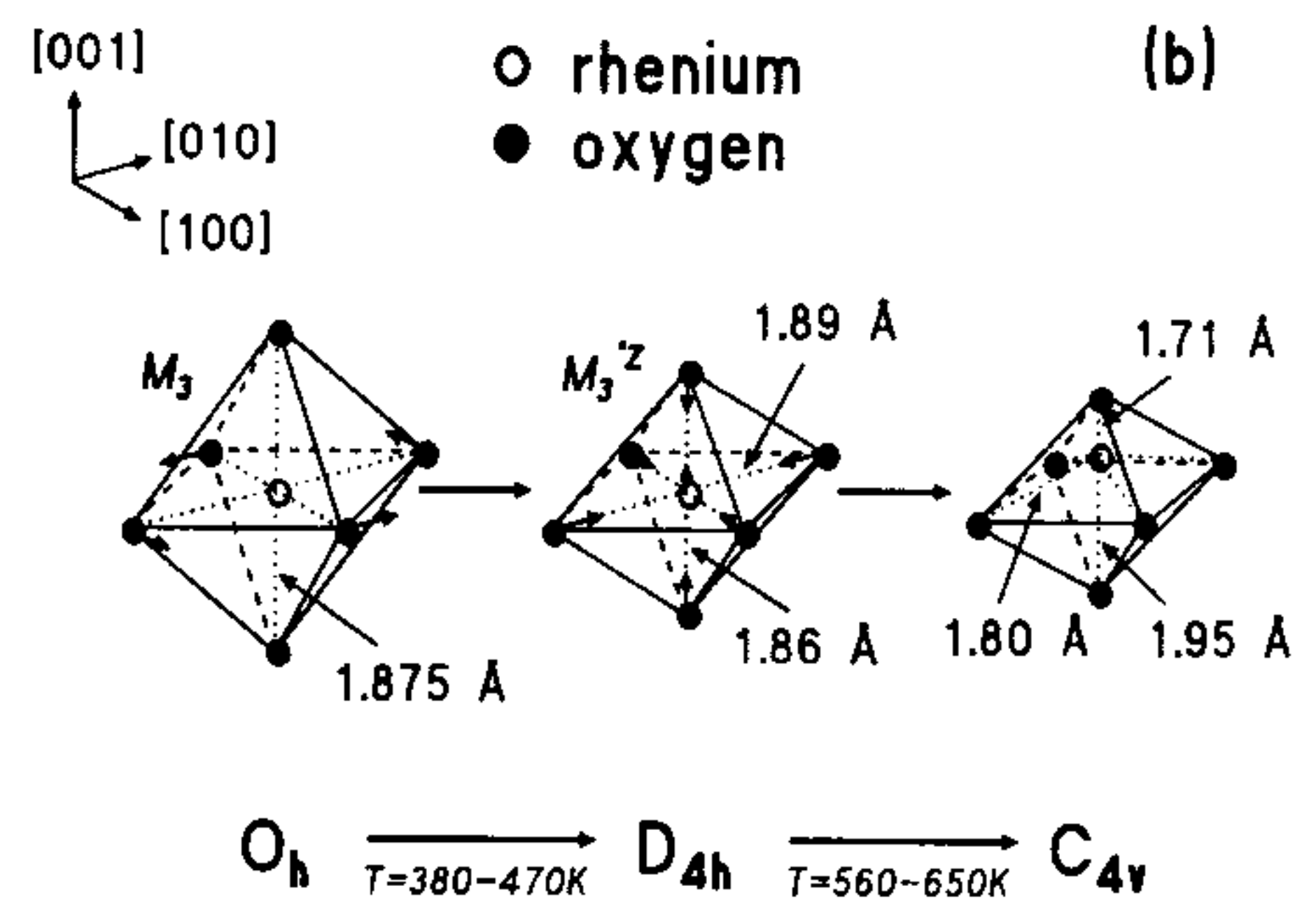
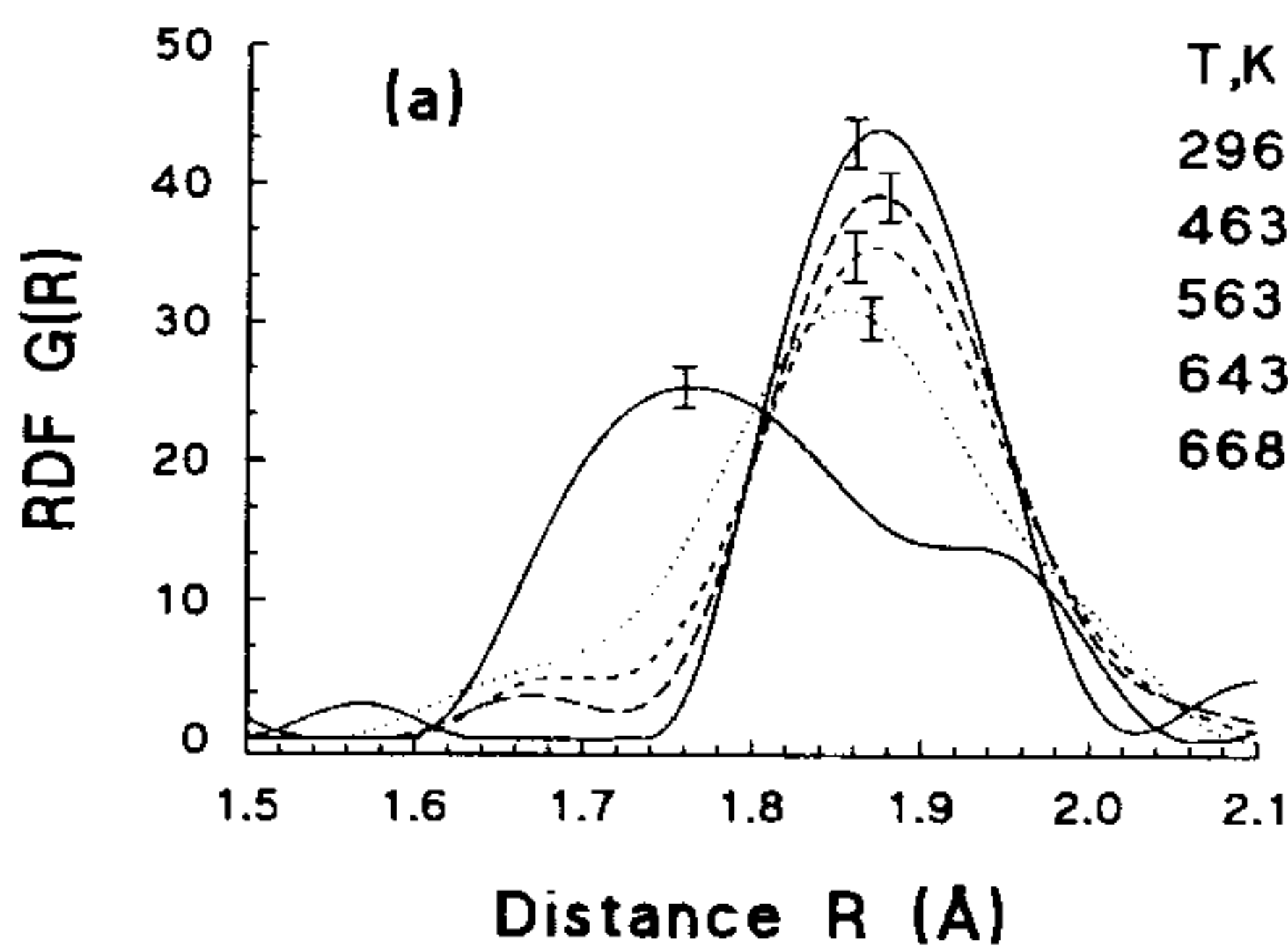


Figure 3: (a) RDF $G(R)$ for the first shell of rhenium in ReO_3 at various temperatures. An asymmetry of the RDF $G(R)$, consisting of the tail at the left side of the peak (at $R \sim 1.7$ Å), progressively increases with temperature passing to the double-peak shape at $T = 668$ K. (b) A model of the high-temperature behaviour of ReO_3 within the first coordination shell: the local symmetry at the rhenium site decreases successively from O_h to D_{4h} and C_{4v} . The rhenium atom is shown by open circle and the oxygen atoms by solid circles. The displacements, caused by the M_3 and M_3^z phonon modes, of oxygen atoms leading to the distortion of the 1st shell are shown by arrows.

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