Investigation of the influence of the isotopic effect on the metal–insulator phase-transition temperature in vanadium oxides

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We investigated the influence of the isotopic effect on the metal–insulator phase-transition temperature in vanadium oxides for the purpose of determining the contribution of the phonon subsystem to the mechanism of phase transitions of this type. It is shown that a regular feature of all the investigated vanadium oxides is a shift of the phase-transition temperature towards higher temperatures when the oxygen O^{16} is replaced by its isotope O^{18}.

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There is a large group of transition-metal and rare-metal compounds in which a metal–insulator phase transition is observed.[1] A feature that distinguishes these compounds from ordinary classical semiconductors is, on the one hand, the presence of a Coulomb interaction between the electrons and, on the other, the interaction of the electrons with the lattice. The relative role of these factors in the interpretation of the metal–insulator phase transition is not clear and is of great interest.

To this end, we have substituted, for the first time ever, the oxygen O^{16} by its isotope O^{18} in the lattices of V_2O_3, V_3O_5 and VO_2 and investigated the influence of the isotopic effect on the phase-transition temperature.

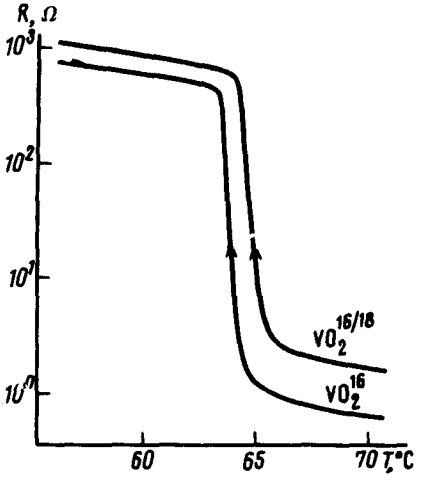

FIG. 1. Temperature dependence of the resistance of the normal and substituted VO_2 samples.

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It is known that the characteristics of transition-metal compounds that undergo a metal–insulator phase transition, particularly the temperature of the phase transition, are strongly influenced by the stoichiometry of the investigated samples, and also by the presence of uncontrollable impurities. In each concrete case, this influence is different and must be taken into account in experiments on substitution of O^{18} for O^{16}. The measures taken for this purpose will be described in a forthcoming paper, where the technology of obtaining samples containing O^{18} will be described.

The influence of the isotopic effect on the temperature of the metal–insulator phase transiton was investigated by the method of differential thermal analysis and by measuring the temperature dependence of the resistance of the investigated substance. The accuracy with which the phase-transition temperature was measured was not worse than ∓ 0.1 °C in both cases.

Figure 1 shows the temperature dependence of the resistance of single crystals VO_2^{16} and $VO_2^{16/18}$ of the upper limit of the homogeneity region. The concentration of the O^{18} ions was $\sim 20\%$ of the total number of oxygen ions. It is seen from the figure that when O^{16} is replaced by O^{18} the temperature of the phase transition shifts towards higher temperatures by (0.8 ± 0.1) °C. In the case of V_2O_3 and V_3O_5 we observed also respectively increase of (2.1 ± 0.1) °C and (0.4 ± 0.1) °C in the temperature of the metal–insulator phase transition.

Thus, the experiments have shown that for all the investigated vanadium oxides there exists a regular shift of the phase-transition temperature towards higher temperatures when O^{16} is replaced by its isotope O^{18}. One cannot exclude the possibility that the temperature shift of the phase transition is a measure of the extent to which the lattice and the electron-phonon interaction participate in the mechanism of the metal–dielectric phase transition, since the concentration of the substituted oxygen ions was approximately the same in all the considered oxides.

We note in conclusion that there is a rather large number of known metal–dielectric phase transition mechanisms but, with a rare exception, the theoretical descriptions of these mechanisms is far from complete and is unfortunately only qualitative in character.[2] The role of the phonons and of the electron-phonon interaction was considered, in particular, in[3,4]. However, the formulas obtained for the temperature of the metal–insulator phase transition in both cases contain both the average frequency of the phonons and the parameter of the electron-phonon interaction, and the estimate of the change of the latter in these compounds following the replacement of O^{16} by O^{18} constitutes apparently the principal difficulty. This makes is impossible, in final analysis, to estimate the expected theoretical effect due to replacement of O^{16} by O^{18} and is apparently the task for further research.

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