Interpretation of lattice-parameter changes accompanying the electrical transition caused by alloying V_2O_3 into Ti_2O_3

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The changes in lattice parameters which occur in the $(Ti_{1-x}V_x)_2O_3$ semiconductor-semimetal system as x is increased from 0 to 0.09 are interpreted in terms of the balance between the reduction in electronic (band) energy and the increase in elastic free energy accompanying strains which affect band overlap. Values are deduced for deformation potentials.

I. INTRODUCTION

The semiconductor-to-semimetal transition[1] which occurs as V_2O_3 is alloyed into Ti_2O_3 is accompanied by changes in the lattice parameters[2,3] and Raman frequencies[4] at room temperature and in the specific heat,[5] the elastic constants,[6] and the magnetic susceptibility[7] measured at low temperatures. Interpretation of the lattice-parameter behavior has been neglected hitherto. It will be the concern of this paper.

II. DISCUSSION

The dependences of various properties on small amounts of V_2O_3 alloyed into Ti_2O_3 have been attributed to changes in the density, and perhaps kind, of electronic energy states at the Fermi level[4,5] and/or to the introduction of impurity states[7,8] (including singly occupied magnetic ones[7]). Thus the distribution of relevant electronic energy levels is more complicated in $(Ti_{1-x}V_x)_2O_3$ than in the case of undoped Ti_2O_3 where the semiconductor-semimetal transition which occurs between about 400 and 500 K has been interpreted simply in terms of the approach and partial overlap of valence and conduction bands.[9]

Nevertheless, it turns out that the behavior of the lattice parameters can be explained simply in terms of the changes in the concentrations of mobile charge carriers attributable to changes in the amount of band overlap produced by varying the V_2O_3 content. This is shown below by comparing theoretical expressions for the strains parallel and perpendicular to the c axis with the strains deduced from lattice parameter versus V_2O_3 content data[3] of Rice and Robinson (RR).

The expressions to be used are like those derived by Keyes[10] for bismuth by minimizing (with respect to strain components) the free energy comprised of (i) the energy associated with how two electronic energy bands near the Fermi energy shift with strain relative to each other in the deformation-potential approximation and of (ii) the elastic free energy including only those strains that can affect the overlap of the two bands. The expressions are

$$\epsilon_{\parallel} = -\Delta N\,(2S_{13}A_1 + S_{33}A_3) \tag{1}$$

and

$$\epsilon_{\perp} = -\Delta N[(S_{11} + S_{12})A_1 + S_{13}S_3]\,, \tag{2}$$

where ΔN is the concentration of mobile charge carriers in each of the two overlapping bands, the S_{ij}'s are elastic compliance constants, and the A_i's are deformation-potential constants defined in terms of the band gap[11,12] in Ti_2O_3, thus causing the negative signs in Eqs. (1) and (2). It will be assumed that ΔN is simply equal to the concentration of vanadium minus the carrier concentration in undoped Ti_2O_3 in view of previous work.[7,13]

TABLE I. Fractional vanadium concentration x, carrier concentration N, excess of carrier concentration over that in Ti_2O_3 ΔN, and elastic compliances S_{ij}.

x	N[a] (10^{20} cm^{-3})	ΔN	S_{13}[b]	S_{33}[b] (10^{-13} cm^2/dyn)	$S_{11}+S_{12}$[b]
0	0.7	0	−2.12	5.77	3.74
0.020	7.6	6.9	−2.56	6.60	4.20
0.040	15.2	14.5	−2.52	6.75	4.10
0.087	33.0	32.3	−2.06	5.88	3.56

[a] Inferred from Refs. 7 and 13.
[b] Deduced from Ref. 14.

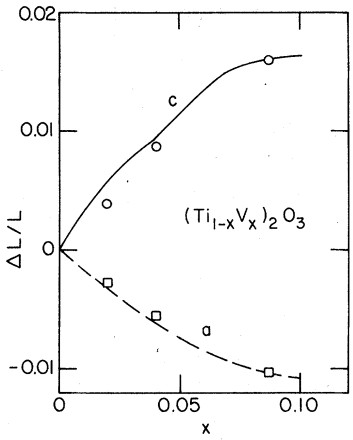

FIG. 1. Fractional changes in c and a lattice parameters as V_2O_3 is alloyed into Ti_2O_3. The curves are deduced from lattice-parameter data of Rice and Robinson at 296 K (Ref. 3 of text). The symbols give values obtained from Eqs. (1) and (2).

The S_{ij}'s can be deduced from elastic constant data.[14] Table I lists the values I used for ΔN and the S_{ij}'s.

To proceed, I required Eqs. (1) and (2) to fit the strains deduced from lattice-parameter data[3] (See Fig. 1) for $x = 0.087$. This yielded $A_1 = 4.1$ eV and $A_3 = -2.3$ eV. Then using these deformation potentials (and appropriate values of ΔN and the S_{ij}'s), I calculated the strains for $x = 0.02$ and 0.04. As can be seen from Fig. 1, they agree very well with those deduced from lattice-parameter data, thus supporting the electronic strain interpretation of the dependence of the lattice parameters on V_2O_3 content.

Values have been obtained for the deformation potentials in semimetallic $(Ti_{1-x}V_x)_2O_3$ previously from elastic constant data at 1.5 K.[6] However, those deformation potentials were deduced using carrier concentrations equal to about 25% of the vanadium concentration.[15] Thus it is not appropriate to compare the deformation potentials in Ref. 6 with the values obtained in this investigation. However, reanalysis[16] of the elastic constant data of Ref. 6 in a manner consistent with the present investigation yields a value for A_3 about equal to that obtained herein and a value of A_1 that is only about one-half of that obtained herein. The value of A_1 recently deduced from elastic constant data does have rather large uncertainty, but not enough to account for the discrepancy of a factor of 2. A possible explanation might be that A_1 has a quite different value at 296 K (deduced herein from lattice-parameter data) than at 1.5 K, where it was deduced from elastic constant data. In view of the agreement of the values for A_3, this seems unlikely.

The deformation potentials obtained herein are in qualitative agreement with (but somewhat larger in magnitude than) those deduced from recent analyses[16,17] of piezoresistivity,[17] elastic constant data,[11] and lattice-parameter data[18] on Ti_2O_3 through its electrical transition. This suggests that there is similar electronic involvement in the transitions produced by doping with V_2O_3 and that caused by increasing the temperature of Ti_2O_3.

III. CONCLUSION

Strain associated with the redistribution of charge carriers between two different groups of electronic energy levels is found to account for how the lattice parameters depend on the amount of V_2O_3 alloyed into Ti_2O_3.

ACKNOWLEDGMENT

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