[2]. The experiments were performed with the solid paraffin at room temperature, which corresponds to a subcooled condition. The results of [2] also indicate that conduction is important only at early times and that natural convection becomes dominant at later times.

REFERENCES

1. E. M. Sparrow, R. R. Schmidt and J. W. Ramsey, Experiments on the role of natural convection in the melting of solids, *J. Heat Transfer* **100**, 11–16 (1978).
2. R. D. White, A. G. Bathelt, W. Leidenfrost and R. Viskanta, Study of heat transfer and melting front from a cylinder imbedded in a phase change material, ASME paper No. 77-HT-42 (1977).

LATTICE THERMAL CONDUCTIVITIES OF TiO—MeO (Me=Ni, Co, Mn) SOLID SOLUTIONS

A. Kh. Muranevich

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem,
Jerusalem, Israel

NOMENCLATURE

k_l, lattice thermal conductivity;
k_0, thermal conductivity of perfect lattice;
ω_D, maximum frequency of Debye spectrum;
ω_0, frequency at which probabilities of umklapp scattering and imperfection scattering are equal;
Γ, scattering parameter;
V, average volume per atom;
N, number of molecules per unit volume;
θ_D, Debye temperature;
M_i, mass of molecule;
$\bar{M}$, average mass of molecules of crystal;
x_i, concentration of molecules of mass M_i;
k_l^I, lattice thermal conductivity calculated for imperfection scattering of phonons by local mass changes;
k_l^{II}, lattice thermal conductivity calculated for imperfection scattering of phonons by local mass and force-constant changes;
g, bond constant of nearest metal and oxygen atoms in host lattice;
g_i, bond constant of impurity atom and its nearest neighbors;
Δg_i, $(g - g_i)$ difference;
γ, Gruneisen parameter;
δ, interatomic distance in host lattice;
δ_i, impurity radius;
$\Delta\delta_i$, $(\delta - \delta_i)$ difference;
α, regulated parameter in Parrott's theory;
B_N and B_U, scattering factors for N-processes and U-processes.

I. INTRODUCTION

Titanium monoxide $TiO_{1\pm x}$ and the iron group metal monoxides $Me_{1-x}O$ (Me=Ni, Co, Mn) have the same crystalline structure (rock salt), but differ considerably in the nature of the interatomic interactions and by the degree of localization of 3d electrons. Accordingly, different TiO—MeO (Me=Ni, Co, Mn) solid solutions formed during the isomorphous substitution of atoms in the metal sublattice have different transport properties, and, in particular, different thermal conductivities.

As reported earlier [1], TiO—MeO (Me=Ni, Co, Mn) solid solutions with a small content of iron group metal atoms have a low lattice thermal conductivity. The electronic and lattice thermal conductivities of these compounds at room temperature are comparable; this is typical of alloys and semimetals containing many imperfections. At high temperatures heat transfer is carried out essentially by free 3d electrons. A similar increase in the electronic contribution to the thermal conductivity with that of temperature was observed in the transition metal carbides and nitrides with high residual electrical resistivities; Williams [2] has explained this effect by the strong scattering of electrons by lattice vacancies. When the concentration of the iron group metal atoms in TiO—MeO (Me=Ni, Co, Mn) solid solutions is increased, the localization of 3d electrons strengthens, so that in solid solutions with a small titanium content the heat is transferred solely by lattice vibrations.

In this paper an analysis of the lattice thermal conductivity data is presented for TiO—MeO (Me=Ni, Co, Mn) solid solutions of different compositions and the phonon scattering processes are considered.

II. EXPERIMENTAL

The experimental details of this study have been described elsewhere [1]. The solid solutions were prepared by the solid-phase reaction method. The composition of the samples and the X-ray and pycnometric data are given in Table 1. The absolute stationary method was used for the thermal-conductivity measurements. The electrical conductivity was measured by the two-probe D.C. potentiometric method.

The lattice thermal conductivities k_l of TiO—MeO (Me=Ni, Co, Mn) solid solutions at room temperature are shown in Fig. 1 and Tables 2 and 3 (for metallic type samples k_l was defined by subtracting the electronic component from the measured total thermal conductivity). A comparison of the above data with the theory of heat transfer in solid solutions is presented below.

III. DISCUSSION OF RESULTS

According to Klemens [3], the thermal conductivity of solid solutions in the case of strong imperfection scattering can be expressed as

$$k_l = k_0 \frac{\omega_0}{\omega_D} \tan^{-1}\left(\frac{\omega_D}{\omega_0}\right) \tag{1}$$

where k_0 is the thermal conductivity of a perfect crystal lattice, ω_D, the maximum frequency of the Debye vibration spectrum and ω_0, the frequency at which the probabilities
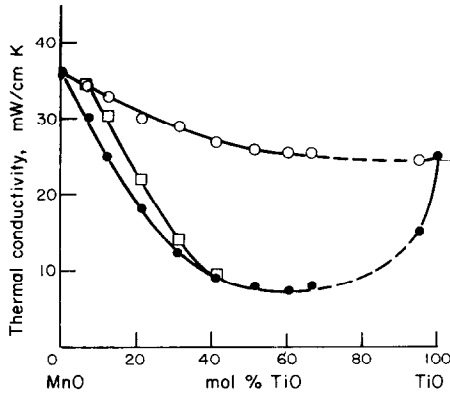
FIG. 1. Lattice thermal conductivities ot TiO—MnO solid solutions at room temperature: ● values of k_l measured or determined from the total thermal conductivity data by subtraction of the electronic component [1]; ○ calculated values k_l^I; □ calculated values k_l^{II}. Dashed curves correspond to the two-phase compositions.

of the umklapp scattering and imperfection scattering are equal.

Using equation (1), we have calculated the lattice thermal conductivities of TiO—MeO (Me=Ni, Co, Mn) solid solutions at room temperature. The quantity $(\omega_D/\omega_0)^2$ was calculated in the form [4]

$$\left(\frac{\omega_D}{\omega_0}\right)^2 = 1.32 \times 10^{13} \frac{k_0\Gamma}{V^{2/3}N\theta_D} \qquad (2)$$

where V is the average volume per atom of the crystal, N, the number of molecules per unit volume, θ_D, the Debye temperature, and the parameter Γ is given by

$$\Gamma = \frac{\sum_i x_i(M_i - M)^2}{\bar{M}^2} \qquad (3)$$

(assuming that the imperfection scattering of phonons results from only local mass changes). There x_i is the concentration of molecules of mass M_i and $\bar{M}$ is the average mass of all molecules. The volume per atom was defined from the X-ray data (Table 1) and the quantities k_0,

N and θ_D for solid solutions were determined by means of linear interpolation between the corresponding values in pure oxides. The Debye temperature of titanium oxide was estimated from the Lindemann rule [4] and melting point data [5]; for the iron group metal oxides we have used the values of θ_D from the paper of Slack and Newman [6].

The calculated values of k_0, θ_D and N are given in Tables 2 and 3. Also presented are the values k_l^I calculated from equations (1)–(3). For TiO—MnO solid solutions the values k_l^I are additionally shown in Fig. 1. As seen, the calculated values k_l^I for all compositions are appreciably higher than the experimental values of k_l. This result seems to be sound, since in solid solutions of the considered type one can expect also local force constant changes. These changes would be greater in the TiO—MnO system, where the lengths of the Ti—O and Mn—O bonds differ to a greater extent than those of the Ti—O and Ni—O bonds and the Ti—O and Co—O bonds (Table 1).

Thus, in the next step, we considered the additional scattering of phonons by local force constant variations. The parameter Γ in this case has the form [7].

$$\Gamma = \sum_i x_i \left\{ \left(\frac{\Delta M_i}{\bar{M}}\right)^2 + 2\left[\left(\frac{\Delta g_i}{g}\right) - 6.4\gamma\left(\frac{\Delta\delta_i}{\delta}\right)\right]^2 \right\}. \qquad (4)$$

The first term represents the mass-defect scattering, g, the bond constant of the nearest metal and oxygen atoms in host lattice, g_i, the bond constant of an impurity atom and its nearest neighbors, γ, the Gruneisen parameter, and δ_i, the impurity radius (of the order of the interatomic distance). For lack of Gruneisen parameter data, we have estimated the lattice thermal conductivity from equation (4) only for solid solutions of composition close to NiO, CoO and MnO. For these compounds we have assumed [6] that γ = 2. The terms g_i and δ_i were defined by linear interpolation between the corresponding values in pure oxides. The bond force constants were calculated from the Gordy formula [8]. We have used the electro-negativity values from the work of Grigorovich [9]. The calculated values of k_l^{II} using this method are given in Tables 2 and 3 and Fig. 1. It can be seen that k_l^{II} exceeds the lattice conductivity k_l for all solid solutions except $Ti_{0.60}Mn_{0.35}O$, $Ti_{0.51}Mn_{0.44}O$ and $Ti_{0.41}Mn_{0.54}O$. The reason for this behavior is an additional phonon scattering. This could be a scattering by normal processes (N-processes) which is disregarded in the Klemens model.

The effect of N-processes on the lattice conductivity was

Table 1. Characterization of the TiO—MeO (Me=Ni, Co, Mn) solid solutions [1]

Composition	a (Å)	Number of atoms in cell	ρ_1 pycnom. (g cm^{-3})	ρ_2 X-ray (g cm^{-3})	ρ_1/ρ_2
$TiO_{1.04}$	4.177	6.54	4.72	5.86	0.81
$Ti_{0.95}Ni_{0.06}O$	4.174	6.57	4.82	5.81	0.83
$Ti_{0.91}Ni_{0.09}O$	4.174	6.56	4.88	5.93	0.82
$Ti_{0.75}Ni_{0.20}O$	4.170	6.73	5.10	6.00	0.85
$Ti_{0.10}Ni_{0.92}O$	4.176	7.29	6.20	6.96	0.89
$Ti_{0.06}Ni_{0.94}O$	4.175	7.51	6.36	6.76	0.94
$Ni_{0.96}O$	4.174	7.84	6.48	6.61	0.98
$Ti_{0.96}Co_{0.05}O$	4.155	6.39	4.80	6.04	0.80
$Ti_{0.88}Co_{0.10}O$	4.158	6.48	4.87	5.95	0.82
$Ti_{0.11}Co_{0.90}O$	4.260	7.62	6.05	6.39	0.95
$Ti_{0.06}Co_{0.95}O$	4.264	7.79	6.24	6.43	0.97
CoO	4.263	7.80	6.27	6.44	0.97
$Ti_{0.95}Mn_{0.05}O$	4.174	6.44	4.74	5.89	0.80
$Ti_{0.41}Mn_{0.54}O$	4.442	7.72	4.91	4.96	0.99
$Ti_{0.31}Mn_{0.63}O$	4.448	7.76	4.90	4.95	0.99
$Ti_{0.21}Mn_{0.74}O$	4.454	7.77	5.00	5.03	0.99
$Ti_{0.12}Mn_{0.88}O$	4.459	7.80	5.15	5.28	0.98
$Ti_{0.07}Mn_{0.93}O$	4.447	7.90	5.28	5.35	0.99
MnO	4.445	7.88	5.30	5.38	0.99

Table 2. Lattice thermal conductivities of the TiO—NiO and TiO—CoO solid solutions

Composition	$k_0 \times 10^3$ (W/cm K)	θ_D (K)	$N \times 10^{-22}$ (1/cm³)	$k_l \times 10^3$ (W/cm K) [1]	$k_l^I \times 10^3$ (W/cm K)	$k_l^{II} \times 10^3$ (W/cm K)	$\alpha = (B_N/B_U)$
$Ti_{0.95}Ni_{0.06}O$	29.7	586	4.5	17.1	29.1		
$Ti_{0.91}Ni_{0.09}O$	32.1	579	4.5	22.2	30.5		
$Ti_{0.75}Ni_{0.20}O$	41.0	547	4.7	30.3	37.7		
$Ti_{0.10}Ni_{0.92}O$	108.2	547	4.9	63.4	95.2	83.3	1.5
$Ti_{0.06}Ni_{0.94}O$	109.5	535	5.1	80.5	102.9	102.9	1.2
$Ti_{0.96}Co_{0.05}O$	26.2	585	4.4	18.1	24.9		
$Ti_{0.88}Co_{0.10}O$	27.5	565	4.5	21.4	26.7		
$Ti_{0.11}Co_{0.90}O$	60.2	513	4.9	34.8	56.6	54.2	1.1
$Ti_{0.06}Co_{0.95}O$	62.2	509	4.9	39.2	59.1	57.8	1.1

Table 3. Lattice thermal conductivities of the TiO—MnO solid solutions

Composition	$k_0 \times 10^3$ (W/cm K)	θ_D (K)	$N \times 10^{-22}$ (1/cm³)	$k_l \times 10^3$ (W/cm K) [1]	$k_l^I \times 10^3$ (W/cm K)	$k_l^{II} \times 10^3$ (W/cm K)	$\alpha = (B_N/B_U)$
$Ti_{0.95}Mn_{0.05}O$	24.6	580	4.4	15.1	24.5		
$Ti_{0.66}Mn_{0.25}O$	26.0	523	4.4	8.1	25.5		
$Ti_{0.60}Mn_{0.35}O$	26.7	517	4.4	7.2	25.6	7.2	
$Ti_{0.51}Mn_{0.44}O$	27.6	506	4.4	8.0	25.9	7.7	
$Ti_{0.41}Mn_{0.54}O$	28.7	495	4.5	9.0	26.9	9.5	
$Ti_{0.31}Mn_{0.63}O$	31.2	500	4.4	12.3	29.0	14.0	0.01
$Ti_{0.21}Mn_{0.74}O$	30.9	471	4.4	18.1	29.9	22.0	0.7
$Ti_{0.12}Mn_{0.88}O$	33.7	482	4.4	24.9	33.0	30.7	0.8
$Ti_{0.07}Mn_{0.93}O$	34.3	476	4.5	30.2	34.3	34.3	0.8

considered by Parrott [10]. He assumed that the relaxation times of normal and umklapp processes (U-processes) have the same dependence on temperature and phonon frequency. In that case, the expression for the lattice thermal conductivity contains a regulated parameter $\alpha = B_N/B_U$ which defines the relative effectiveness of N-processes in comparison to U-processes (B_N and B_U are the corresponding scattering factors). The values of α, estimated by us according to the Parrott model, provide qualitative information on the effect of N-processes on the lattice conductivity of the solid solutions under consideration. In the row of TiO—NiO, TiO—CoO and TiO—MnO solid solutions, the contribution of N-processes to phonon scattering decreases (Tables 2 and 3). This is probably connected with the fact that, as mentioned above, the imperfection scattering of phonons due to the local force constant variations strengthens in this row.

REFERENCES

1. M. I. Aivazov, A. Kh. Muranevich and I. A. Domashnev, Thermal conductivities of TiO—MeO (Me=Ni, Co, Mn) solid solutions, *High Temperature* 11(2), 271–775 (1973).
2. W. S. Williams, High temperature thermal conductivity of transition metal carbides and nitrides, *J. Am. Ceram. Soc.* 49(3), 156–159 (1966).
3. P. G. Klemens, Thermal resistance due to point defects at high temperatures, *Phys. Rev.* 119(2), 507–509 (1960).
4. J. R. Drabble and H. J. Goldsmid, *Thermal Conduction in Semiconductors*, pp. 191–192. Pergamon Press, New York (1961).
5. I. I. Kornilov and V. V. Glazova, *Reactions of Refractory Metals of Transition Groups with Oxygen* (in Russian). Nauka, Moscow (1967).
6. G. A. Slack and R. Newman, Thermal conductivity of MnO and NiO, *Phys. Rev. Lett.* 1(10), 359–360 (1958).
7. P. G. Klemens, The scattering of low-frequency lattice waves by static imperfections, *Proc. Phys. Soc. Lond.* A68, 1113–1128 (1955).
8. W. Gordy, A relation between bond force constants, bond orders, bond lengths, and the electronegativities of the bonded atoms, *J. Chem. Phys.* 14(5), 305–320 (1946).
9. V. K. Grigorovich, *Study of Metals in Solid and Liquid States* (in Russian). Nauka, Moscow (1964).
10. J. E. Parrott, The high temperature thermal conductivity of semiconductor alloys, *Proc. Phys. Soc. Lond.* A81, 726–735 (1963).