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Thermal Constants for Ni, NiO, MgO, MnO and CoO at Low Temperatures

H. Watanabe

General Education, Osaka Sangyo University, 3-1-1, Nakagaito, Daito 574 (Japan)

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ABSTRACT

Thermal diffusivities and specific heat capacities for nickel (Ni), nickel oxide (NiO), magnesium oxide (MgO), manganese oxide (MnO) and cobalt oxide (CoO) were measured in the temperature range 120 K to 480 K using a laser flash calorimeter. Values of thermal conductivities for the above five materials were calculated from the measured thermal diffusivity values and specific heat capacity values. Cobalt oxide has a thermal diffusivity minimum and a thermal conductivity maximum at 287 K as well as a specific heat capacity maximum as results of the magnetic transition.

INTRODUCTION

Manganese oxide (MnO), cobalt oxide (CoO) and nickel oxide (NiO) have a pronounced specific heat capacity maximum at 117.8 K (Todd and Bonnickson, 1951), at 287.3 K (King, 1957) and at 523.16 K (Tomlinson et al., 1955), respectively. Although we can find specific heat capacity data for the above materials in many literatures, there are a few data of thermal diffusivities and thermal conductivities except those for magnesium oxide (MgO). This paper presents the results of thermal diffusivity and specific heat capacity measurements for Ni, NiO, MgO, MnO and CoO at low temperatures 120 K to 480 K and the calculated values of thermal conductivities for the above five materials.

MATERIALS

Nickel sample was commercially pure (99.9 %), supplied by Ohji Alloy Corp., Tokyo, Japan. Nickel oxide (NiO), magnesium oxide (MgO), manganese oxide (MnO) and cobalt oxide (CoO) were single crystals (99.99 % pure) grown by a flame fusion method by Earth Jewelry Corp., Osaka, Japan. A shape of sample used for the measurements was a small disk, 10 mm in diameter and 2 to 3 mm in thickness. Physical characteristics for the above five samples are listed in Table 1.

TABLE 1

Physical characteristics of five samples at room temperature

Sample	Density (g/cm^3)	Mass (g)	Thickness (mm)
Ni	8.85	1.3435	1.920
NiO	6.80	1.5006	2.682
MgO	3.58	0.7715	2.890
MnO	5.36	1.1655	2.649
CoO	6.43	1.3926	2.645

MEASUREMENTS

We used a Rigaku Model PS-7 laser flash calorimeter. The light source was a ruby laser. The energy of its flash light was about 10 Joules and its duration time was about 850 microseconds. The temperature in a sample chamber was controlled with an electric furnace which was in the outer cryostat. Temperature of a disk sample was measured with a platinel thermocouple which was attached to the back surface of the sample with a platinum paste. The surface of the sample was blackened with a quick drying carbon spray. The atmosphere in the sample chamber was made a good vacuum with a rotary pump, 10^{-3} Torr. Temperature range measured was 120 K to 480 K.

The flash method was first described by Parker et al. (1961). Values of thermal diffusivity, α, and specific heat capacity, C_p, are determined from the following equations, respectively,

$$\alpha = \frac{1.37L^2}{\pi^2 t_{1/2}} \tag{1}$$

$$C_p = \frac{Q}{m\Delta T} \tag{2}$$

where $t_{1/2}$ is the time required for the back surface of the sample to attain half its maximum increase in temperature, ΔT, Q is the energy absorbed by the front surface of the sample, L is the thickness of the sample and m is the mass. Values of thermal conductivities, k, are calculated from

$$k = \alpha C_p \rho \tag{3}$$

where ρ is the density of the sample. In this study, values of thermal conductivity for five materials were calculated from the measured values of thermal diffusivity and specific heat capacity, assuming the density of the sample to be constant throughout the temperature range studied.

RESULTS

Measured values of thermal diffusivities, α, and specific heat capacities, C_p, and calculated values of thermal conductivities, k, for nickel (Ni), nickel oxide (NiO), magnesium oxide (MgO), manganese oxide (MnO) and cobalt oxide (CoO) at low temperatures 120 K to 480 K are listed in Table 2. Present values of thermal diffusivities and specific heat capacities are mean values obtained by several runs at the same temperature, and those are precise to ±5 % throughout the temperature range studied.

TABLE 2

Thermal diffusivities, α, specific heat capacities, C_p, and thermal conductivities, k, for five materials at low temperatures 120 K to 480 K

T	α	C_p	k	T	α	C_p	k
K	$\times 10^{-6}$ m^2/s	J/kgK	W/mK	K	$\times 10^{-6}$ m^2/s	J/kgK	W/mK
Nickel (Ni)				Nickel oxide (NiO)			
133.0	28.9	310	79.3	135.7	32.8	330	73.6
143.7	27.9	324	80.0	147.6	30.0	360	73.4
151.0	27.3	334	80.7	159.3	26.7	390	70.8
162.9	26.3	348	81.0	177.7	22.7	420	64.8
173.8	25.6	358	81.1	187.7	20.9	435	61.8
189.5	24.9	375	82.6	199.2	18.7	460	58.5
196.2	24.4	380	82.1	206.7	17.7	470	56.6
209.5	23.4	391	81.0	220.3	15.9	485	52.4
238.1	22.3	405	79.9	229.0	14.6	495	49.1
260.0	21.3	423	79.7	250.5	12.4	528	44.5
281.6	20.6	435	79.3	263.9	11.2	548	41.7
291.8	20.2	440	78.7	277.2	9.80	565	37.7
327.4	19.1	455	76.9	294.8	8.80	590	35.3
362.4	18.2	470	75.7	325.2	7.32	621	30.9
398.0	17.3	485	74.3	349.8	6.47	645	28.4
408.3	17.0	490	73.7	371.4	5.70	668	25.9
436.7	16.3	501	72.3	397.3	5.07	690	23.8
446.7	16.0	504	71.4	419.0	4.62	710	22.3
451.7	15.9	508	71.5	450.0	4.01	750	20.5
479.0	15.4	520	70.9	477.8	3.60	782	19.1
Magnesium oxide (MgO)				Manganese oxide (MnO)			
127.7	46.9	400	67.2	125.0	2.90	445	6.92
130.1	45.6	410	66.9	134.0	2.84	455	6.23
149.1	37.1	491	65.2	149.0	2.71	477	6.93
170.9	31.0	580	64.4	174.3	2.57	512	7.05
198.7	25.0	685	61.3	191.6	2.45	536	7.04
218.9	22.0	750	59.1	201.8	2.40	546	7.02
228.9	20.8	781	58.2	210.8	2.37	560	7.11
242.3	19.2	810	55.7	230.8	2.30	581	7.16

249.5	18.0	835	53.8	242.6	2.23	591	7.06
266.1	16.7	871	52.1	258.3	2.16	603	6.98
273.2	16.2	889	51.6	270.2	2.12	611	6.88
293.6	14.4	935	48.2	291.9	2.06	625	6.90
317.3	12.8	975	45.0	303.7	2.01	632	6.81
331.7	11.8	991	41.9	322.5	1.95	641	6.70
341.9	11.4	1001	40.8	340.2	1.88	647	6.52
366.2	10.2	1031	37.6	364.9	1.81	655	6.35
392.6	9.23	1055	34.9	387.4	1.76	660	6.23
419.5	8.59	1080	33.2	414.4	1.70	667	6.08
449.8	7.95	1093	31.1	440.1	1.64	671	5.90
473.6	7.50	1115	29.9	473.3	1.59	675	5.75

Cobalt oxide (CoO)

120.6	6.25	400	16.1	287.4	1.57	950	9.59
132.1	5.51	435	15.4	290.2	1.65	760	8.06
149.7	4.50	483	14.0	294.3	1.81	740	8.61
169.1	3.60	535	12.6	298.1	1.96	728	9.17
187.5	3.10	581	11.6	303.7	2.11	724	9.82
208.9	2.65	638	10.9	331.6	2.04	715	9.38
221.5	2.40	670	10.3	358.1	1.95	714	8.95
240.1	2.07	723	9.62	377.2	1.89	713	8.66
254.9	1.85	765	9.10	398.2	1.83	713	8.39
269.3	1.67	820	8.81	420.7	1.75	714	8.03
280.4	1.54	875	8.66	453.7	1.68	712	7.69
285.6	1.45	975	9.09	475.9	1.63	715	7.49

Thermal diffusivities

Sidles and Danielson (1960) have reported the thermal diffusivity data for Ni at temperatures 273 K to 1273 K, Makarounis and Jenkins (1962) those for a single crystal of MgO at low temperatures 94 K to 487 K, and Kanamori et al. (1968) those for a single crystal of MgO at high temperatures 400 K to 1100 K. The values of present mesurements for Ni, NiO, MgO, MnO and CoO are plotted in Fig. 1.

Values of thermal diffusivity for NiO are smaller than those for MgO by 20 to 50 percent throughout the temperature range measured and the temperature variation for NiO is similar to that for MgO and much greater than that for Ni. Values of thermal diffusivities for MnO and CoO are much smaller than those for Ni, NiO and MgO by one order of magnitude. The temperature variation for MnO is similar to that for Ni. CoO has the most pronounced temperature variation at temperatures lower than 287 K and the gentlest one at temperatures higher than 304 K. Minimum thermal diffusivity for CoO is 1.45×10^{-6} m^2/s at 287 K and its maximum is 2.11×10^{-6} m^2/s at 304 K. These anomalous changes are a result of the magnetic transition between antiferromagnetic and paramagnetic phases at 287 K.

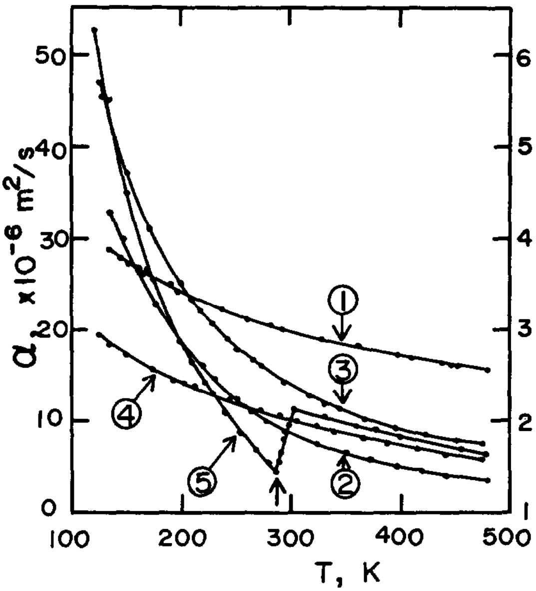

Fig. 1. Temperature variations of thermal diffusivities, α, for Ni (curve 1), NiO (2), MgO (3), MnO (4) and CoO (5). Right vertical scale is for MnO and CoO. Magnetic transition temperature of CoO is indicated by an arrow.

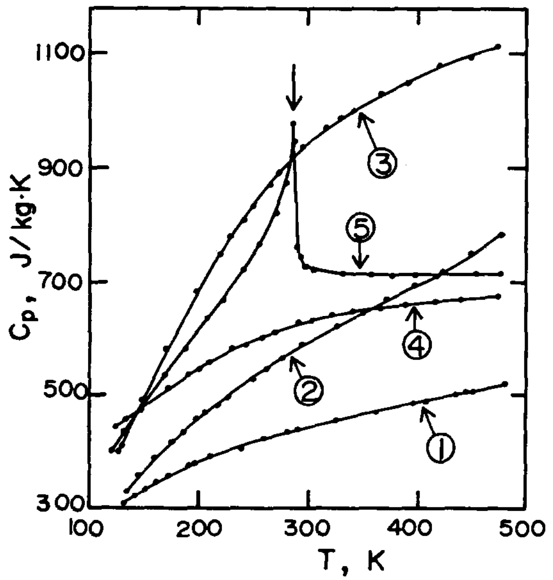

Fig. 2. Temperature variations of specific heat capacities, C_p, for Ni (curve 1), NiO (2), MgO (3), MnO (4) and CoO (5). Magnetic transition temperature of CoO is indicated by an arrow.

Specific heat capacities

Specific heat capacity data for the five materials studied have already reported by many authers; for Ni by Busey and Giaque (1952) and Pawel (1956), for NiO by King (1957) and Tomlinson et al. (1955), for MgO by Barron et al. (1959) and Victor and Douglas (1960), for MnO by Todd and Bonnickson (1951) and Watanabe (1982), for CoO by King (1957), King and Christensen (1958) and Watanabe (1982). Values of the present measurements for Ni, NiO, MgO, MnO and CoO are plotted in Fig. 2. These values determined by the flash method agree well with the reported ones determined by the adiabatic method and by the DSC method within the experimental errors.

Temperature variation of specific heat capacity for CoO near the magnetic transition temperature, Néel temperature, was determined in different runs. The measured values are tabulated in Table 3 and plotted in Fig. 3. Maximum specific heat capacity determined is 1006 J/kgK at 286.8 K in the first run and 1000 J/kgK at 286.8 K in the second one. These values agree well with the reported one; 17.6 cal/molK, i.e. 983 J/kgK, at 287.3 K (King, 1957).

TABLE 3

Spesific heat capacities, C_p, for CoO near the magnetic transition temperature, 287 K, in different runs

Temperature (K)	C_p (J/kgK)	Temperature (K)	C_p (J/kgK)
1st run		2nd run	
279.7	870	278.2	866
281.0	880	279.7	875
283.2	908	280.7	884
283.6	923	281.4	891
285.7	974	282.1	903
286.8	1006	284.0	912
287.7	902	285.1	929
288.3	825	285.7	962
288.6	771	286.4	989
290.0	759	286.8	1000
291.2	754	289.5	807
292.8	746	290.0	792
293.6	742	290.6	772
		292.3	753

Thermal conductivities

Although we can find previous measurements of thermal conductivities for Ni reported by Moss (1955), and for single crystals of NiO and MnO by Slack and Newman (1958), there are a few data except those for a single crystal of MgO (see Touloukian et al., 1970). Calculated values of thermal conductivities in this study for Ni, NiO, MgO, MnO and CoO are plotted in Fig. 4. Temperature variations for Ni and MnO are the smallest, those for NiO and MgO are intermediate, and that for CoO is the most pronounced at temperatures lower than 287 K. Values for MnO and CoO are much smaller than Ni, NiO and MgO by one order of magnitude. Conductivity curve for CoO has a complex temperature variation near the magnetic transition temperature, 287 K; i.e. double minima at 280 K and 290 K and double maxima at 287 K and 304 K. These anomalous changes in thermal conductivity for CoO as well as those in thermal diffusivity and specific heat capacity are the results of the magnetic transition, Néel transition.

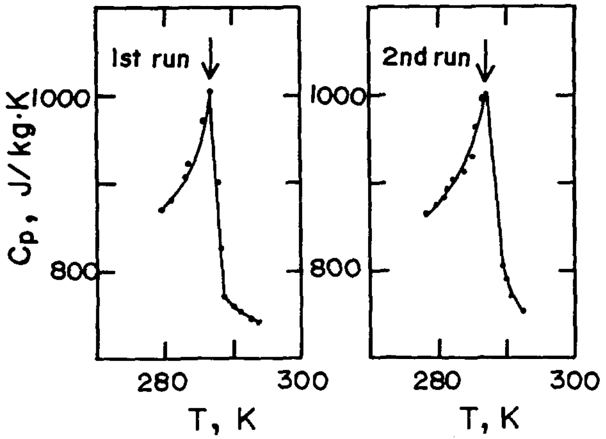

Fig. 3. Temperature variations of specific heat capacities, C_p, for CoO near the Néel temperature, which is indicated by an arrow.

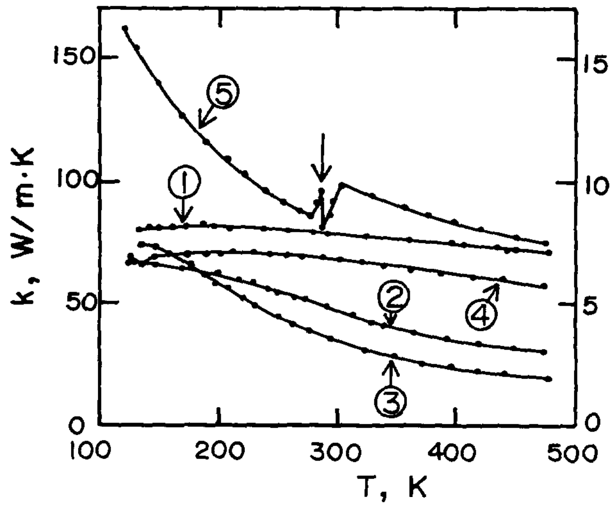

Fig. 4. Temperature variations of thermal conductivities, k, for Ni (curve 1), NiO (2), MgO (3), MnO (4) and CoO (5). Right vertical scale is for MnO and CoO. Néel temperature of CoO is indicated by an arrow.

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