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Thermal Conductivity of La_2CuO_4, La_2NiO_4, and Nd_2CuO_4 in the Semiconducting and Metallic Phases

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Thermal conductivity of polycrystalline La_2CuO_4, La_2NiO_4, and Nd_2CuO_4 was measured in the temperature range 300–1000 K. No anomaly in thermal conductivity has been observed during the semiconductor-to-metal transition of La_2NiO_4 or in the metallic phases of La_2CuO_4 and La_2NiO_4. A change of slope has been found, however, in the thermal conductivity of La_2CuO_4 at the crystallographic transition. The thermal conductivity of the oxides is mainly phononic in this temperature range.

KEY WORDS: electrical conductivity; La_2CuO_4; La_2NiO_4; Nd_2CuO_4; oxides; phonons; thermal conductivity; thermal expansion.

1. INTRODUCTION

In recent years, materials showing transition from semiconductor to metal, or vice versa, have received considerable attention. These materials, while passing through the transition, exhibit changes in their crystal structure, electrical transport, and magnetic properties, which are well studied [1]. However, adequate attention has not been given to their thermal transport properties. A few references [2–4] appearing in the literature are ambiguous in as much as their nature and mode of heat conduction during or after the transition. For example, the thermal conductivity of vanadium oxide reported by Bergland and Guggenheim [2] did not show any change during the phase transition; the conductivity was found to be temperature independent. However, the measurement by Andreev et al. [3] on VO_2, V_2O_3, and V_3O_5 revealed a drop in their conductivity at the transition, which thereafter resembled that observed for amorphous materials.

Rare earth oxides of the general formula Ln_2XO_4 (Ln = La, Nd and

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X = Cu, Ni) have been studied extensively with respect to their electrical transport properties [5–7], magnetic properties [8–10], and crystallographic transitions [11, 12]. Because of the complexity in the structural arrangement of atoms, these oxides exhibit varied behavior in their properties [13]. Thus La_2CuO_4 is metallic even at room temperature, La_2NiO_4 shows a semiconductor $\rightleftharpoons$ metal transition at about 600 K, and Nd_2CuO_4 is semiconducting. An orthorhombic-to-tetragonal crystallographic transition is reported for La_2CuO_4 at about 533 K [11]. However, their thermal transport properties have not been studied so far. The aim of the present work is to investigate the nature of their thermal conductivity in the semiconducting and metallic phases and also during the phase transitions. In order to determine the contributions of the different factors to the total thermal conductivity, their electrical conductivity, linear thermal expansion, and specific heat variations have been measured in the same temperature interval.

2. EXPERIMENTAL

The compounds were prepared by solid-state reactions of the respective oxides. Powders of the component oxides of a putity greater than 99.9% were mixed thoroughly and heated initially in a platinum crucible in air at 1250 K for a period of 10 h. The product was ground and reheated till the compounds were formed, which were characterized by X-ray diffraction using CuK_α radiation.

Sintered samples were prepared for the measurements by uniaxial cold compaction of the oxides followed by sintering at 1400 K in air for 48 h. For all measurements, two pellets were prepared from two different lots. The density of the samples varied between 70 and 80% of the theoretical. All the measurements were carried out in air from 300 to 1000 K.

The thermal conductivity was measured on pellets 2.5 cm in diameter and 2–3 cm in height by the comparative method, described elsewhere [14]. Pyroceram-9606 and Inconel-718 were used as standards. The accuracy of the measurements was better than $\pm 5\%$.

The thermal expansion was measured on samples 1.25 cm in diameter and 1.00 cm in thickness using quartz push-rod dilatometer (Model LKB-3185) with a calibrated dial gauge. The accuracy of the dial gauge was $\pm 0.5\ \mu m$.

Measurement of the electrical conductivity of the samples was carried out by a four-probe DC cell [15].

DSC measurements were made on La_2CuO_4 and La_2NiO_4 between 300 and 750 K, with a differential scanning calorimeter (Perkin–Elmer DSC-1B).

3. RESULTS AND DISCUSSION

Figure 1 shows the variation of the measured thermal conductivity of La_2CuO_4, La_2NiO_4, and Nd_2CuO_4 with the inverse of temperature, corrected for zero porosity using the equation of Franel and Kingery [16]. Typical data obtained on two samples for each oxide are presented in Tables I, II, and III. It is found that the thermal conductivity of the oxides decreases with an increase in temperature.

The results of the electrical conductivity measurements are shown in Fig. 2, which are in good agreement with those reported in the literature [5–7]. The plots clearly show the metallic nature of La_2CuO_4, the semiconducting behavior of Nd_2CuO_4, and the semiconductor-to-metal

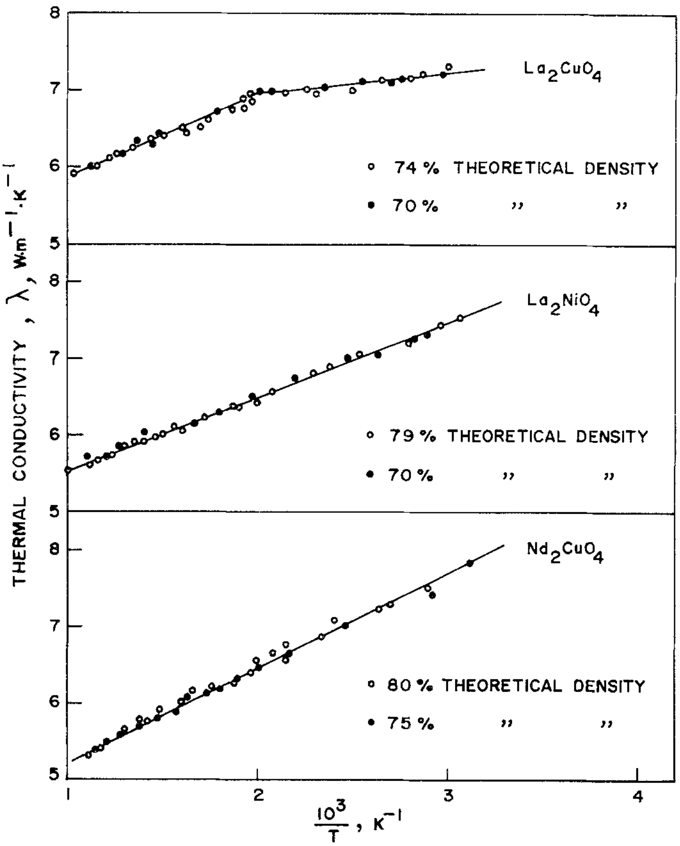

Fig. 1. Thermal conductivity of La_2CuO_4, La_2NiO_4, and Nd_2CuO_4, corrected for porosity, as a function of inverse temperature.

transition of La_2NiO_4. The data are employed for calculation of the electronic contribution to the thermal conductivity (λ_e).

The percentages linear thermal expansion of the oxides as a function of temperature are shown in Fig. 3. A change of slope is observed at about 530 K in the case of La_2CuO_4, while the DSC measurements did not

Table I. Measured Values of Thermal Conductivity of La_2CuO_4

Sample	Standard used: Inconel-718 Temp. (K)	Inconel-718 λ ($W \cdot m^{-1} \cdot K^{-1}$)	Pyroceram-9606 Temp. (K)	Pyroceram-9606 λ ($W \cdot m^{-1} \cdot K^{-1}$)
I	360	5.29	330	5.39
(74% theoretical density)	370	5.25	350	5.32
	400	5.18	375	5.25
	440	5.17	430	5.14
	465	5.14	510	5.07
			590	4.82
	510	5.14	620	4.81
	520	4.98	690	4.66
	530	4.96	735	4.63
	575	4.88	790	4.50
	615	4.76	845	4.45
	665	4.75	915	4.37
	695	4.70		
	740	4.66		
	795	4.55		
	820	4.52		
	865	4.44		
	960	4.36		
	1000	4.33		
II	335	5.05	395	5.00
(70% theoretical density)	365	5.00	630	4.50
	425	4.92	735	4.45
	485	4.98	855	4.20
	500	4.90	895	4.20
	560	4.69		
	580	4.67		
	675	4.50		
	780	4.28		
	790	4.37		
	870	4.13		

indicate any noticable change in the specific heat of the samples in the temperature interval of measurements.

The thermal conductivity of semiconductors represents the cumulative transport of heat by phonons (λ_p) and by electrons and holes (λ_e). Quantitative expressions for estimating the phononic contribution of thermal

Table II. Measured Values of Thermal Conductivity of La_2NiO_4

	Standard used			
	Inconel-718		Pyroceram-9606	
	Temp. (K)	λ ($W \cdot m^{-1} \cdot K^{-1}$)	Temp. (K)	λ ($W \cdot m^{-1} \cdot K^{-1}$)
I	325	5.96	335	5.88
(79% theoretical density)	360	5.70	395	5.56
	420	5.46	435	5.37
	480	5.17	505	5.10
	500	5.06	510	5.13
	530	5.02	530	4.98
	560	4.96	580	4.88
	605	4.86	605	4.82
	645	4.82	625	4.76
	685	4.69	660	4.75
	720	4.66	675	4.70
	740	4.68	705	4.69
	765	4.62	745	4.57
	800	4.54	790	5.53
	835	4.50	865	4.47
	865	4.46	895	4.47
	915	4.42		
	1005	4.35		
II	345	5.11	355	5.09
(70% theoretical density)	375	4.90	405	4.91
	505	4.48	455	4.73
	620	4.34	505	4.57
	720	4.22	550	4.41
	815	3.99	600	4.34
	850	4.05	675	4.33
			710	4.21
			750	4.13
			795	4.10
			850	4.05
			895	3.99

conductivity (λ_p) have been proposed by various investigators [17–19]. Even though these expressions are essentially equivalent in nature, the computed numerical values differ considerably [19, 20]. Hence instead of calculating λ_p numerically, its relation with temperature was evaluated using the expression given by Dugdale and McDonald [18]:

$$\lambda_p = \frac{1}{3}\frac{cva}{\alpha r T} \tag{1}$$

Table III. Measured Values of Thermal Conductivity of Nd_2CuO_4

	Standard used			
	Inconel-718		Pyroceram-9606	
	Temp. (K)	λ $(W \cdot m^{-1} \cdot K^{-1})$	Temp. (K)	λ $(W \cdot m^{-1} \cdot K^{-1})$
I	345	5.88	345	6.00
(80% theoretical density)	380	5.79	385	5.67
	425	5.48	390	5.78
	465	5.26	405	5.60
	510	5.15	480	5.33
	530	5.04	490	5.16
	565	4.95	500	5.26
	625	4.82	530	5.00
	675	4.73	575	4.97
	725	4.58		
	765	4.52		
	815	4.41		
	875	4.32		
	925	4.20		
	965	4.20		
	1000	4.16		
II	320	5.88	345	5.53
(75% theoretical density)	370	5.47	405	5.26
	405	5.25	430	5.10
	465	5.03	505	4.83
	525	4.73	535	4.73
	555	4.65	580	4.64
	610	4.58	635	4.43
	675	4.43	685	4.35
	720	4.31	730	4.28
	780	4.20	780	4.20
	835	4.13	815	4.13
	910	3.98	860	4.04
			900	3.98

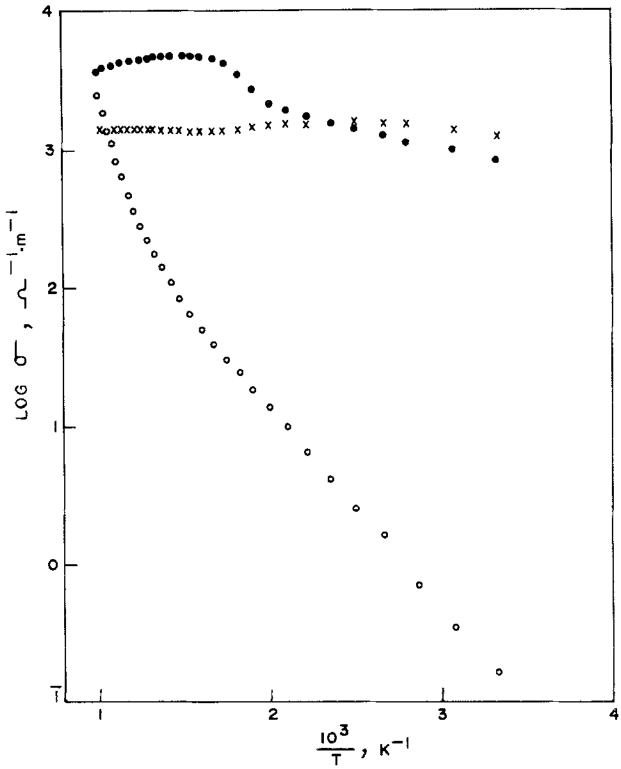

Fig. 2. Electrical conductivity (σ) of La_2CuO_4 (×), La_2NiO_4(●), and Nd_2CuO_4 (○) versus inverse temperature.

where c is the lattice specific heat per unit volume, v is the velocity of sound in the medium, a is the lattice constant, r is the Grüneisen constant, and α is the linear thermal expansion coefficient. From the above expression, it can be noted that unless any or all the terms involved in the equation show an abrupt change with temperature other than the usual monotonic variations, λ_p will be inversely dependent on T.

Prior investigations [11, 12] have shown that there is no major change in the lattice constants of these oxides with temperature, even in the case of La_2CuO_4 during the crystallographic transition. As described previously, DSC did not show any change in the specific heat of the samples. In the case of thermal expansion, the plot showed a change of slope for La_2CuO_4, corresponding to its crystallographic transition, and no such change was observed for the other oxides. The velocity of sound in the oxides and their Grüneisen constants have been assumed to be constant [21]. Thus, in these oxides the various terms in Eq. (1) are not

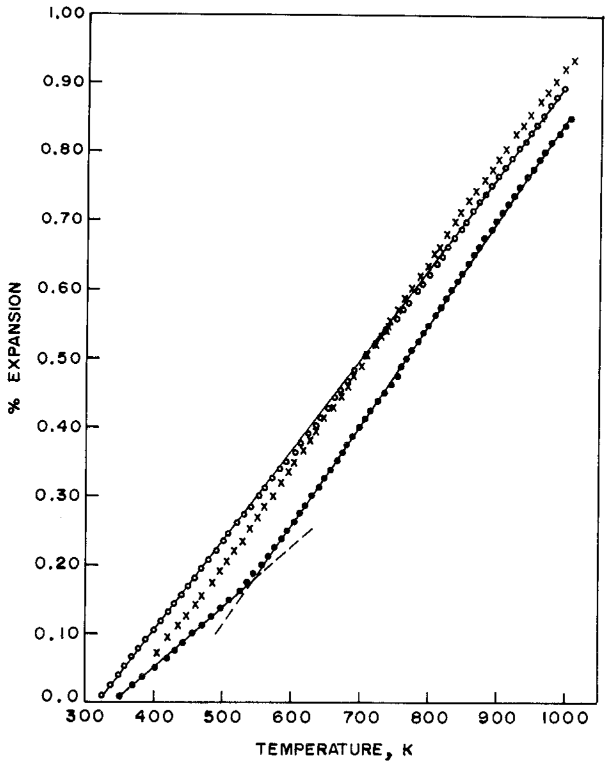

Fig. 3. Percentage expansion of La_2CuO_4 (●), La_2NiO_4 (○), and Nd_2CuO_4 (×) as a function of temperature.

significantly affected by temperature. Under these conditions λ_p exhibits an inverse relation with temperature. The plots of the measured thermal conductivity with the inverse of temperature (Fig. 1) are linear in all cases, thereby showing that the thermal conductivity of the oxides is predominantly phononic.

The electronic part of the thermal conductivity (λ_e), calculated using the Wiedmann–Franz equation [22], and the measured electrical conductivity are given in Table IV. λ_e is observed to be negligible compared to the total thermal conductivity. Unlike in the case of the metallic phases of vanadium oxides, the conductiviries of La_2CuO_4 and La_2NiO_4 are inversely dependent on temperature in the metallic phases; there is no evidence to suggest that any other conduction mechanism is operative in this range. The changes in the slope of the plot of λ verses $1/T$ above and below the crystallographic transition in La_2CuO_4 are a direct result of the corresponding dependence of the linear thermal expansion on temperature.

Table IV. Measured Values of Electrical Conductivity (σ) and Calculated Values of Electronic Thermal Conductivity (λ_e)

Temp. (K)	La_2CuO_4 $\sigma \times 10^{-2}$ $(\Omega^{-1} \cdot m^{-1})$	La_2CuO_4 $\lambda_e \times 10^2$ $(W \cdot m^{-1} \cdot K^{-1})$	La_2NiO_4 $\sigma \times 10^{-2}$ $(\Omega^{-1} \cdot m^{-1})$	La_2NiO_4 $\lambda_e \times 10^2$ $(W \cdot m^{-1} \cdot K^{-1})$	Nd_2CuO_4 σ $(\Omega^{-1} \cdot m^{-1})$	Nd_2CuO_4 $\lambda_e \times 10^3$ $(W \cdot m^{-1} \cdot K^{-1})$
300	12.690	0.933	8.503	0.625	0.170	0.001
325	14.306	1.139	10.122	0.806	0.347	0.003
350	15.601	1.339	11.521	0.988	0.761	0.007
375	15.823	1.454	12.987	1.193	1.677	0.015
400	15.949	1.563	14.104	1.382	2.565	0.025
425	15.748	1.640	15.773	1.642	4.307	0.045
450	15.480	1.707	17.452	1.924	6.865	0.076
475	15.337	1.785	19.646	2.286	10.015	0.117
500	15.038	1.842	22.173	2.716	13.877	0.170
525	14.620	1.881	28.249	3.634	18.473	0.238
550	14.265	1.922	36.232	4.882	24.041	0.324
575	13.986	1.970	43.103	6.072	30.193	0.425
600	13.947	2.050	46.083	6.774	38.685	0.569
625	13.661	2.092	47.619	7.292	49.628	0.760
650	13.680	2.179	48.309	7.693	66.370	1.057
675	13.774	2.278	48.309	7.990	86.957	1.438
700	13.831	2.372	48.077	8.245	111.645	1.915
725	14.327	2.545	47.619	8.458	139.373	2.477
750	14.306	2.629	47.170	8.668	175.438	3.224
775	14.389	2.732	46.083	8.750	221.631	4.208
800	14.306	2.804	45.455	8.909	278.862	5.466
825	14.265	2.883	44.643	9.024	367.377	7.426
850	14.245	2.967	43.668	9.094	484.731	10.095
875	14.205	3.045	43.103	9.240	638.978	13.698
900	14.144	3.119	41.667	9.188	846.024	18.655
925	14.045	3.183	41.600	9.428	1149.425	26.049
950	13.967	3.250	40.761	9.487	1497.006	34.843
975	13.793	3.295	40.161	9.593	1949.318	46.564
1000	13.736	3.365	38.314	9.387	2487.562	60.945

4. CONCLUSIONS

The thermal conductivities of La_2CuO_4, La_2NiO_4, and Nd_2CuO_4 are identical and comparable in magnitude even though they exhibit diverse electrical transport properties. Phonons are found to be the predominant carriers of heat, and the heat conduction is not affected by the semiconductor–metal transition in La_2NiO_4. The crystallographic transition in La_2CuO_4 is clearly reflected in its thermal conductivity.

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REFERENCES

1. D. Adler, *Rev. Mod. Phys.* **40**:714 (1968).
2. C. N. Bergland and H. J. Guggenheim, *Phys. Rev.* **185**:1022 (1969).
3. V. N. Andreev, F. A. Chudnoskii, A. V. Petrov, and E. I. Terukov, *Phys. Stat. Sol. (a)* **48**:K153 (1978).
4. M. B. Salamon, J. W. Bray, G. De Pasquali, and R. A. Craven, *Phys. Rev. B* **11**:619 (1975).
5. M. Foex, *Bull. Soc. Chim. France* **109** (1961).
6. P. Ganguly and C. N. R. Rao, *Mat. Res. Bull.* **8**:405 (1973).
7. A. M. George, I. K. Gopalakrishnan, and M. D. Karkhanavala, *Mat. Res. Bull.* **9**:721 (1973).
8. R. Saez Puche, M. Norton, and W. S. Glaunsinger, *Mat. Res. Bull.* **17**:1429 (1982).
9. R. Saez Puche, M. Norton, and W. S. Glaunsingar, *Mat. Res. Bull.* **17**:1523 (1982).
10. G. A. Smolenskii, V. N. Yudin, and E. Sher, *Sov. Phys. Solid State* **4**:2452 (1963).
11. J. M. Longo and P. M. Raccah, *J. Solid State Chem.* **6**:526 (1973).
12. J. B. Goodenough and S. Ramasesha, *Mat. Res. Bull.* **17**:383 (1982).
13. J. B. Goodenough, *Mat. Res. Bull.* **8**:423 (1973).
14. C. G. S. Pillai and A. M. Gearge, Report BARC-1122 (1981).
15. A. M. George and I. K. Gopalakrishnan, *J. Phys. E. Sci. Instr.* **8**:13 (1975).
16. J. Franel and W. D. Kingery, *J. Am. Ceram. Soc.* **37**:99 (1954).
17. G. Leibfried and E. Schlomann, *Nachr. Ges. Wiss. Goett. Math. Phys.* **K1.2**(4):71 (1954).
18. J. S. Dugdale and D. K. C. Mac Donald, *Phys. Rev.* **98**:1751 (1955).
19. M. Roufosse and P. G. Klemens, *Phys. Rev. B* **7**:5379 (1973).
20. J. E. Parrott and A. D. Stuckes, *Thermal Conductivity of Solids* (Pion, London, 1975), pp. 114–115.
21. C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1966), pp. 183–187.
22. P. E. D. Morgan, *J. Am. Ceram. Soc.* **58**:349 (1975).