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NOTE

Thermal Conductivity of $LaCoO_3$

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The thermal conductivity of $LaCoO_3$ was measured in air between 300 and 900 K. The conductivity increased sharply from 3.2 to 17.0 $W \cdot m^{-1} \cdot K^{-1}$ in this temperature range and showed good agreement with previously published data. An excitonic mode of conduction due to the interaction of the high-low spin states of cobalt is found to be the main contribution to the measured thermal conductivity. Contributions of the other modes of conduction and the excitonic mean free path have been calculated.

KEY WORDS: $LaCoO_3$; thermal conductivity.

1. INTRODUCTION

The electrical conductivity of $LaCoO_3$ [1, 2] has been widely investigated. It shows high electrical conductivity, even at room temperature, which is attributed to the formation of high-spin Co^{3+} in the oxide. It undergoes a semiconductor-metal transition at about 1210 K [3]. Gerthsen and Kettle [4] studied the thermal and electrical conduction in pure and Th and Sr substituted $LaCoO_3$ from 140 to 750 K. These authors explained the thermal conductivity data on the basis of an excitonic mode of heat conduction and calculated the diffusion coefficient and enthalpy of formation of the excitons. The present study was carried out primarily to ascertain the contributions of the other modes of conduction to the total thermal conductivity of $LaCoO_3$ and also to examine the data of the previous authors.

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2. EXPERIMENTAL PROCEDURE

The compound was prepared by heating a mixture of lanthanum oxalate and Co_3O_4 in the required proportion. Both the reactants were of purity 99.9% or higher. The mixture of reactants was initially heated at 1000 K for a period of 8 h. The product was then ground and reheated at 1400 K for an additional period of 10 h. The process was repeated a few times to ensure the completion of the reaction. The compound was characterized by X-ray diffraction using CuK_α radiation.

Cylindrical specimens of $LaCoO_3$, about 3×10^{-2} m in length and 3×10^{-2} m in diameter, were obtained by cold compaction of the as-prepared oxide, under a load of 5000 kg, followed by sintering in air at 1600 K. The sintered blocks were thereafter annealed at 1200 K for 50 h and shaped to the required dimensions by lapping. The bulk density of the specimens was about 75% of the theoretical.

The thermal conductivity of the samples was measured by the comparative method [5]. Details of the experimental procedure have been reported elsewhere [6]. Measurements were carried out on two samples using different standards. The overall accuracy of the measurements was ±5%.

3. RESULTS AND DISCUSSION

The experimental data of the thermal conductivity (Table I) were corrected for porosity using the equation of Franel and Kingery [7] and are given in Fig. 1 as a function of temperature. The thermal conductivity of the compound rapidly increases with temperature. The present data are in good agreement with those of Gerthsen and Kettle [4], albeit, a little on the high side. This deviation can be understood if their data are corrected for sample porosity corresponding to 65% of theoretical density.

In the temperature range investigated, $LaCoO_3$ is a semiconductor, and hence various carriers such as phonons, electrons, and holes and their pairs can contribute to the thermal conductivity. The electronic part of the thermal conductivity (λ_e) arising from electrons and holes is estimated using the Wiedemann–Franz equation [8, 9]:

$$\lambda_e = L\sigma T \qquad (1)$$

where L is the Lorenz number, σ is the electrical conductivity, and T is the absolute temperature. λ_e is found to increase with temperature from 0.003 $W \cdot m^{-1} \cdot K^{-1}$ at 450 K to about 0.8 $W \cdot m^{-1} \cdot K^{-1}$ at 900 K, as shown in the Fig. 1.

Table I. Measured Values of Thermal Conductivity of $LaCoO_3$

Sample	Standards used	Temp. (K)	λ ($W \cdot m^{-1} \cdot K^{-1}$)
I (70% theoretical density)	Inconel-718	350	2.60
		565	4.50
		665	6.12
		835	9.95
		885	11.50
	Pyroceram-9606	490	3.80
		745	7.93
	Pyrex-7740	520	4.00
		595	5.20
II (76% theoretical density)	Pyroceram-9606	330	2.54
		370	2.80
		455	3.67
		555	5.14
		620	6.50
		830	11.00
	Pyrex-7740	475	4.20
		685	7.60
	Inconel-718	520	4.50
		600	6.00
		780	10.00
		875	12.29

The contribution from ambipolar conduction (λ_{amb}) also shows an increase with temperature. λ_{amb} was calculated using the equation [10]:

$$\lambda_{\text{amb}} = \left(\frac{k}{e}\right)^2 \sigma T \left[\frac{b}{(1+b)^2}\right]\left(4 + \frac{E_g}{kT}\right)^2 \tag{2}$$

where k is the Boltzmann constant, e is the electronic charge, b is the hole to electron mobility ratio, and E_g is the energy of formation of electron-hole pairs. E_g has been computed from our electrical conductivity data [11] and found to be 0.39 eV. The mobility ratio was taken to be 13.3 [12] and was assumed to be constant throughout the temperature range. λ_{amb} at 600 K is only about 10% of the measured value and decreases sharply above this temperature since E_g tends to zero beyond this temperature.

In spite of the substantial increase in the thermal conductivity of $LaCoO_3$ at high temperature, the phononic contribution (λ_{ph}) cannot be overlooked. This contribution has been estimated by extrapolating the low

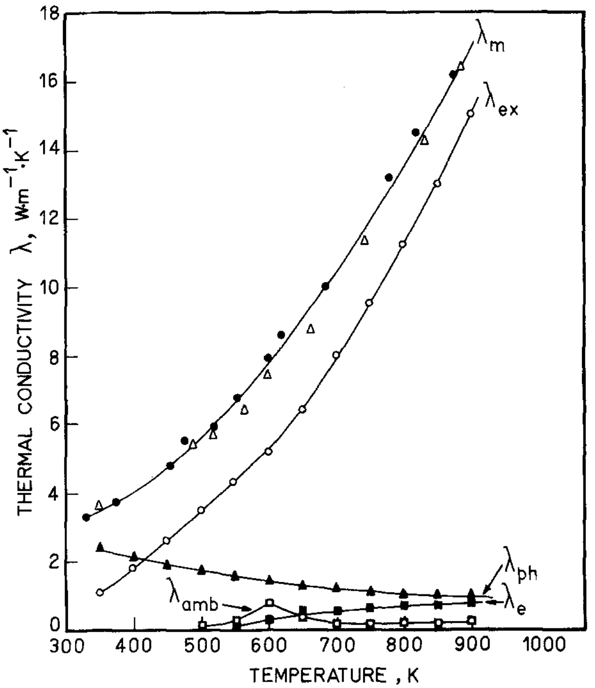

Fig. 1. Measured and calculated thermal conductivities of $LaCoO_3$.

temperature data of Gerthsen and Kettle [4] after applying a porosity correction to their values. The extrapolated phononic conductivity decreases from about 50% at 400 K to 6% at 900 K of the measured value.

Excitonic heat conduction invoked by Gerthsen and Kettle seems to be the appropriate mechanism to explain the rapid increase of λ with temperature. The simultaneous presence of high and low spin states of Co^{+3} ions in $LaCoO_3$ and the temperature dependent conversion of low spin to high spin states and vice versa, presents a highly favorable situation for the formation of excitons. Exciton formation in $LaCoO_3$ by the association of e_g electrons with t_{2g} holes has been explained by Raccah and Goodenough [3]. The diffusion of an exciton along the temperature gradient transports an energy equivalent to its formation energy, E_{ex}.

Assuming the interaction of different carriers to be weak, their contribution to the total thermal conductivity can be considered to be additive; i.e.,

$$\lambda_m = \lambda_{ph} + \lambda_e + \lambda_{amb} + \lambda_{ex} \tag{3}$$

where λ_m is the measured thermal conductivity. Using the data for λ_{ph}, λ_e,

Table II. Mean Free Path of Excitons in $LaCoO_3$

Temp. (K)	l_{ex} (10^{-8} m)
350	3.00
400	2.82
450	2.64
500	2.47
550	2.26
600	2.00
750	1.98
800	1.95
850	1.925
900	1.905

and λ_{amb}, calculated as discussed above, the excitonic conductivity, λ_{ex}, was calculated from the above equation. The contributions of the different modes of conduction are also shown in Fig. 1.

From the excitonic conductivity the exciton mean free path was calculated using the equation of Pikus [13]:

$$\lambda_{ex} = \frac{16\pi}{3}\left(\frac{k}{h}\right)^3 m_{ex}T^2 l_{ex} \exp\left(\frac{-E_{ex}}{kT}\right)\left[\left(\frac{E_{ex}}{kT}+2\right)^2+2\right] \tag{4}$$

where m_{ex} is the mass of the exciton, l_{ex} is its mean free path, h is Planck's constant, and the other symbols have the same meaning as given in Eq. (2). Assuming the excitons to be nonlocalized, m_{ex} is taken to be $2m_0$, where m_0 is the electron rest mass [14]. E_{ex} is taken to be 0.1 eV [4]. The calculated values of mean free path are found to be in the range of 10^{-8} m in the temperature interval and are given in Table II. These values are in good agreement with those reported in the literature for olivine and indium antimonide [14].

4. CONCLUSIONS

The thermal conductivity of $LaCoO_3$ is predominantly excitonic at high temperature, the exciton mean free path being of the order of 10^{-8} m. The assumptions made in the calculation of ambipolar conductivity, that formation energy and mobility ratio of charge carriers are constant, might have introduced some error in the values; the error, however, was estimated to be within the limits of accuracy of the present measurements. The estimated photon contribution in this temperature range was quite insignificant and hence not included in the calculations.

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