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## THERMAL CONDUCTIVITY OF MnO AND NiO<sup>†</sup>

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Thermal conductivity measurements were made on single crystals of MnO and NiO which were grown by the Verneuil process. The crystals were in the shape of rods about 0.5 cm in diameter and were cut to be about 2 cm long. The singleness of the crystals was judged from the fact that they possess well defined orthogonal cleavage faces, and that preliminary x-ray study revealed no large-angle grain boundaries or twins. Neither crystal was annealed after the growing and cutting operations, therefore some strains may be present. No study has been made of the dislocation density. The crystal structure of the monoxide has been verified by x-ray studies. However, small deviations from stoichiometry may exist in these crystals. No intentional impurities were added during growth. The starting material for the NiO was reagent grade NiCO<sub>3</sub>, and reagent grade MnCO<sub>3</sub> was used for the MnO.

The thermal conductivity was measured over the temperature range from 3°K to 300°K. A steady-state heat-flow method was used in which heat was supplied electrically to a nichrome wire heater at the top of the crystal. The temperature gradient along the crystal was measured with a Au + 2.1 atomic percent Co<sup>1</sup> versus Manganin differential thermocouple cemented to the crystal at two points along its length. The thermocouple output was measured using a potentiometer or a direct-current breaker amplifier. A second differential thermocouple measured the temperature difference between the lower point and the base of the crystal. The average temperature at the base of the crystal was measured with a constant volume helium gas thermometer. With this method the thermal resistance of the

contacts at the ends of the sample does not enter the computation of the thermal conductivity. Depending on the temperature range, the heat input to the sample was varied from 0.2 milliwatts to 500 milliwatts, and the temperature gradient from 0.3 deg/cm to 7 deg/cm. The estimated accuracies of the measurements are  $\pm 0.5\%$  for the absolute temperature,  $\pm 3\%$  for the relative thermal conductivity values of a given sample, and  $\pm 8\%$  for the absolute thermal conductivity values. The main error in the absolute values is caused by the somewhat irregular geometry of the sample.

The measured thermal conductivities are shown in Fig. 1. Some tentative explanation of the

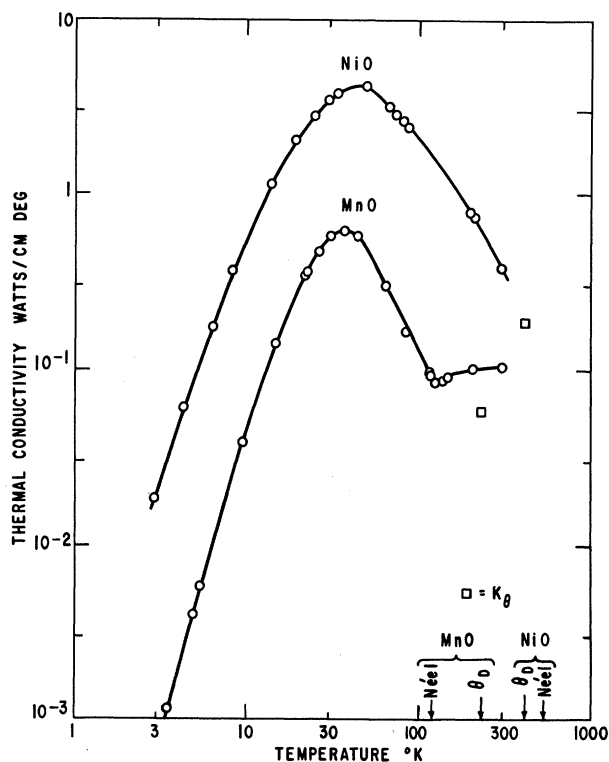


FIG. 1. The thermal conductivity of MnO and NiO versus temperature from 3°K to 300°K.

shapes and magnitudes of these curves can be made. Since the electrical resistivity of both crystals was greater than  $10^5$  ohm cm at all temperatures, only the lattice conductivity should be important. The magnitude of the thermal conductivity at the Debye temperature,  $K_\theta$ , can be estimated.<sup>2</sup> A value of  $\gamma=2$  is assumed for the Grüneisen constant of both materials, and a Debye temperature of 410°K is used<sup>3</sup> for NiO and 230°K for<sup>4</sup> MnO. This gives  $K_\theta=0.19$  watt/cm deg for NiO and 0.059 watt/cm deg for MnO. As seen from the graph, the order of magnitude agreement is satisfactory. The  $K_\theta$  values are calculated assuming that Umklapp-processes are the only mechanism producing thermal resistance. This is clearly not the case in MnO where there is a decided minimum in the thermal conductivity curve at the Néel temperature (120°K) at which MnO changes from an antiferromagnetic state to a paramagnetic one. The lattice distortion<sup>5</sup> which occurs at the Néel point seems to be too small to explain this effect. In addition to the Umklapp scattering, it appears that there is an additional interaction between the phonons and the magnetic moments of the manganese atoms which serves to scatter the phonons. A similar minimum in the thermal conductivity of single crystals of NiO might also be found at its Néel temperature (525°K). Earlier investigations<sup>6</sup> on compressed powder samples of NiO failed to exhibit such a minimum.

Since the thermal conductivity is proportional to the specific heat, one might expect to find a  $\lambda$ -type anomaly in the thermal conductivity similar to that found<sup>4</sup> in the specific heat at the Néel temperature. Although such an anomaly was looked for very carefully during the thermal conductivity measurements, none was found. This indicates that the thermal conductivity associated with the magnetic ordering anomaly in the specific heat curve is less than a few percent of the lattice thermal conductivity at the Néel point.

The thermal conductivity of a perfect insulating crystal at low temperatures should be determined by boundary scattering<sup>7</sup> of the phonons. The magnitude of the boundary scattering has been estimated using the sample diameter, the Debye temperature, and the average sound velocity calculated from the Debye temperature. For NiO with an average velocity of  $2.9 \times 10^5$  cm/sec the result is  $K = 0.11 T^3$  watt/cm deg<sup>4</sup>. The observed  $K$  at the lowest temperatures varies as  $T^3$ , but is a factor of 140 less than the calculated value. This indicates an equivalent mean free

path for the phonons of 30 microns. For MnO the average velocity is  $1.7 \times 10^5$  cm/sec, which gives  $K=0.34 T^3$  watt/cm deg<sup>4</sup>. Since the observed  $K$  is nearly proportional to  $T^3$ , the data indicates a mean free path of 0.5 microns. Thus the external boundaries are not limiting the thermal conductivity at low temperatures; some other scattering mechanism is required to explain the results. This may be the interaction with strains, precipitates, spin waves, or antiferromagnetic domain walls. Further experiments using annealed crystals and crystals grown by other techniques are underway in an attempt to clarify the problem.

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<sup>1</sup> Powell, Rogers, and Coffin, *J. Research Natl. Bur. Standards* **59**, 349 (1957).

<sup>2</sup> G. Leibfried and E. Schlömann, *Nachr. Akad. Wiss. Göttingen, Math.-physik Kl.* **4**, 71 (1954).

<sup>3</sup> Seltz, Dewitt, and McDonald, *J. Am. Chem. Soc.* **62**, 88 (1946); R. R. Wenner, *Thermochemical Calculations* (McGraw-Hill Book Company, New York, 1941), p. 146.

<sup>4</sup> R. Millar, *J. Am. Chem. Soc.* **50**, 1875 (1928).

<sup>5</sup> M. Foex, *Compt. rend.* **227**, 193 (1948); N. C. Tombs and H. P. Rooksby, *Nature* **165**, 442 (1950).

<sup>6</sup> Kingery, Franel, Coble, and Vasilos, *J. Am. Ceram. Soc.* **37**, 107 (1954).

<sup>7</sup> H. B. G. Casimir, *Physica* **5**, 495 (1938).

## LATTICE VIBRATIONAL SPECTRA OF Si AND Ge

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There are two basic ways at the moment for obtaining the lattice vibrational spectrum of a crystal if one has the experimentally determined dispersion relations for the elastic waves traveling in certain directions in the crystal. One is based on an interpolation method which reconstructs the whole vibrational spectrum from the behavior of the dispersion curves at certain singular points in the Brillouin zone<sup>1-3</sup>; the