

## Thermionic Emission from Nickel Oxide

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We have determined the thermionic parameters—true work function,  $A$  constant, and normal energy distribution—for near stoichiometric NiO. The distribution was found to be Maxwellian, with the electron temperature matching the lattice temperature closely. The results show that the Fermi level in NiO is rather insensitive to temperature from room to incandescent temperatures and that the emission probably originates from the itinerant 4s band.

We wish to report the results of our recent thermionic emission experiments using atomically clean, single-crystal NiO cathodes cut approximately normal to the [125] direction.

No single-crystal thermionic emission work pertaining to this interesting transition-metal monoxide has as yet appeared in literature and our results contribute the thermodynamic entities, work function and electron distribution, to the present knowledge of the physical properties of this interesting magnetic insulator in which charge-carrier transport still remains a puzzling and controversial phenomenon even after more than three and a half decades of intensive research.

The method used to measure the temperature dependence of the work function and the normal energy distribution of the emitted electrons was first published by Shelton.<sup>1</sup> He used it to analyze the emission from tantalum; and subsequently Kisliuk,<sup>2</sup> Webster,<sup>3</sup> Busch and Madjid,<sup>4</sup> and Abey<sup>5</sup> employed it in conjunction with electron emission measurements on tungsten, cesiated tantalum, silicon, and tungsten-rhenium alloys, respectively.

The nickel-oxide cathodes were wire sawed, to an approximate dimension 2 cm × 0.25 cm × 0.05 cm, from a Verneuil-grown, single-crystal boule.<sup>6</sup> The original material had a room-temperature resistivity of  $1 \times 10^7 \Omega \text{ cm}$ , but after a heat treatment in vacuum, to reduce excess oxygen content, the wafers turned a light green, and the resistivity of the samples increased to  $7 \times 10^{10} \Omega \text{ cm}$  throughout the bulk, which is a resistivity value that is characteristic of near stoichiometric NiO grown by the halide decomposition method. The cathodes were indirectly heated using platinum and iridium heating elements. The surfaces were cleaned by flashing the cathodes above 1800°K. Two desorption peaks were observed during flashing at 950 and at 1700°K, with respective monolayer times of about 1000 and 300 min at the background pressure in the  $10^{-10}$ -Torr range. Most

of the data were taken within 1/25 of the shorter of the two monolayer times. The temperature of all cathodes was determined pyrometrically using the spectral emissivity values of nickel oxide<sup>7</sup> and tantalum<sup>8</sup> determined by Martinez and Madjid.

The “unknown” (Shelton tube<sup>1</sup>) nickel-oxide surface was used both as an emitter and as a collector. The “standard” surface, also used as an emitter and as a collector, was a single-crystal (110) tantalum surface grown in our laboratory<sup>8</sup> from high-purity tantalum stock. The work function of the tantalum surface was accurately determined previous to this experiment, and it was known that it would emit and absorb virtually a pure Maxwellian energy distribution corresponding to the measured temperature of the surface.

Normal procedures in the Shelton method, which are described in Refs. 1–5, were used to obtain and to analyze the data. The room-temperature work function, both for “clean” and “contaminated” NiO, was obtained by using the tantalum as the emitter and the nickel oxide as the collector. “Clean” refers to a freshly flashed surface with less than 1/25 of one monolayer residual ambient absorbed onto it, and “contaminated” refers to NiO that was exposed to the residual ambient for many monolayer times after being initially flash cleaned. To obtain the high-temperature work-function values, the NiO was used as the emitter and the tantalum crystal as the collector.

The results of the measurements are shown in Table I and in Figs. 1 and 2. Table I compares the temperature determined from the measured distribution with the true temperature of the NiO sample measured pyrometrically. The agreement is excellent, showing that the electron temperature equals the lattice temperature. Figure 1 shows a representative distribution run with the NiO crystal emitting and the Ta crystal collecting. The transmission coefficient over vir-

TABLE I. Comparison between the electron temperature of the emitted electrons, as determined from the measured energy distribution, and the lattice temperature of the NiO cathode which was pyrometrically established.

Electron temperature (°K ± 2°)	Lattice temperature (°K ± 10°)	Difference (°K)
1517	1484	+33
1572	1537	+35
1634	1595	+39
1694	1653	+41
1773	1727	+46

tually the entire measured range of energies is unity except for electrons which are emitted with energies that are less than a few tenths of an electron volt. This can be inferred from the saturation break, which is slightly rounded instead of being sharp. Such reflection effects are caused by a moderate work-function inhomogeneity of the surface. The degree of rounding observed for NiO is not excessive and such rounding is, indeed, often characteristic even of single-crystal cathodes of good quality refractory metal. Figure 2 shows the temperature dependence of the work function. For the high-temperature points the NiO emitted to the Ta collector, and for the room-temperature point the NiO collected the distribution emitted by the tantalum. In the temperature range  $1500 < T < 1800^\circ\text{K}$ , the true work function  $\omega(T)$  of the (125) NiO face shows a linear temperature dependence and may be expressed by

$$\omega(T) \pm 0.02 \text{ eV} = 5.43 - 1.2 \times 10^{-4} T; \quad (1)$$

and the  $A$  value determined was  $480 \pm 100 \text{ A/cm}^2 \text{ }^\circ\text{K}^2$ , from which we may infer that the roughness factor of geometrical area to true area for the samples is about 5, which is reasonable.

What is surprising (in view of the controversy existing ever since the pioneering publication by de Boer and Verwey<sup>9</sup> three and a half decades ago about the nature of the transport in nickel oxide) is the fact that the present thermionic results turned out to be straightforward to interpret, and that they are, in fact, very similar—except for the numerical value of the work function, which is about 1 eV larger—to the results for refractory metals. The temperature coefficient of the work function,  $-1.2 \times 10^{-4} \text{ eV/}^\circ\text{K}$ , is moderate and is comparable to that found in valency semiconductors where it is attributable to temperature-induced lattice dilatation and band-

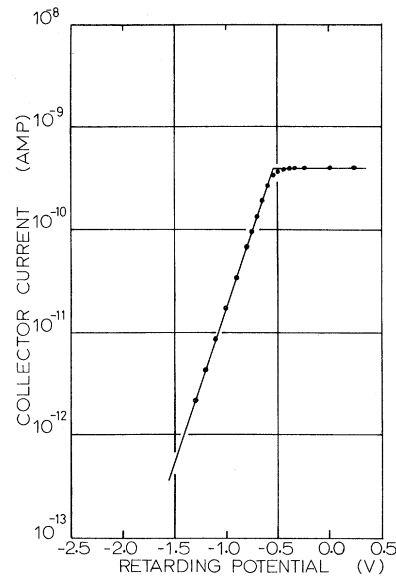


FIG. 1 Representative normal-energy distribution of electrons emitted from the (125) NiO face at  $1572^\circ\text{K}$ .

broadening contributions arising from temperature-dependent, electron-lattice interaction terms. Because the Fermi energy is the negative of the work function if energy is measured from the zero level, the small variation in  $\omega(T)$  also shows that between 1500 and  $1800^\circ\text{K}$  the Fermi level for nickel oxide is temperature invariant to the same order as in ordinary intrinsic Bloch-Wilson model semiconductors. Indeed, al-

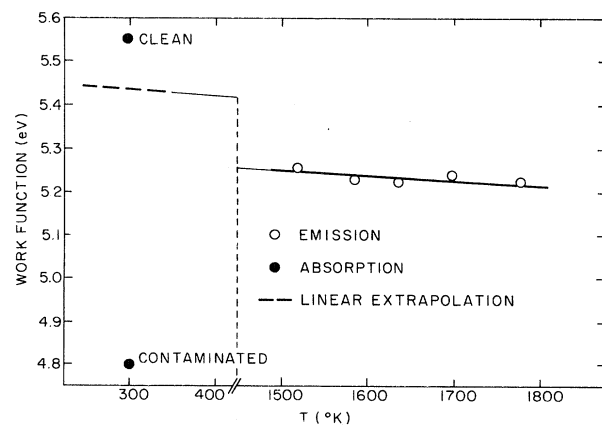


FIG. 2. Dependence of the work function of the (125) NiO face on temperature. Closed circles, measurements in which the NiO is the collector; open circles, measurements in which the NiO is the emitter. "Clean" data were obtained by flashing the NiO above  $1800^\circ\text{K}$ , and "contaminated" data resulted from NiO surfaces exposed for many monolayer times to the vacuum ambient.

though the present measurements did not extend to temperatures between 300 and 1500°K, the linear extrapolation of  $\omega(T)$  from high temperatures misses the measured value of  $\omega(T)$  at room temperature by only 0.1 eV and this might mean that the relative insensitivity of the Fermi level may even persist down to 300°K. The normal energy distribution is strictly Maxwellian and certainly is indistinguishable from that emitted from an itinerant electron gas; and it is tempting to speculate, within this context, whether emission from local states or within a hopping regime would not tend to introduce structure into the distribution due to surface reflection effects,<sup>4,10</sup> that are introduced when matching the wave functions of the emitted electrons through the surface. As it is, the numerical value of the work function determined, and the character of the distribution measured, strongly implies that the thermionic emission in NiO originates from the itinerant 4s band in the band scheme, as published by Adler and Feinleib.<sup>11,12</sup> But, the question as to what measure the 4s band is populated from the localized 3d narrow band<sup>9</sup> or the 2p itinerant band is yet beyond the resolution of this experiment.

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## Improved Kinetic Theory of Sound Propagation\*

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The phase velocity and absorption coefficient in a gas of Maxwell molecules (inverse fifth-power repulsion) are determined to high order in the frequency. A nonlinear transformation of the partial sums for the velocity and absorption series is shown to yield sequences which seem to converge rapidly, and the results are in good agreement with experiment over a wide range of frequencies.

It is well known that the kinetic theory of sound propagation leads to a perturbed eigenvalue problem involving the linearized Boltzmann collision operator, and that it has special significance for testing the Boltzmann equation.<sup>1</sup> For the somewhat unrealistic but mathematically tractable case of Maxwell molecules, the frequency dependence of the phase velocity  $U$  and the absorption

coefficient  $\alpha$  are given by

$$U_0/U = \sum (-1)^n a_{2n} \xi^{2n}, \quad (1)$$

$$\alpha U_0/\omega = \sum (-1)^n a_{2n+1} \xi^{2n+1}, \quad (2)$$

where the dimensionless constants  $a_k$  are determined by the successive orders of the perturbation calculation, and where  $\xi = \mu\omega/\rho U_0^2$ , with  $\mu$