

Electrical and Thermoelectric Properties of Undoped MnO Single Crystals

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The electrical resistivity and Seebeck coefficients of pure MnO single crystals have been measured above the Néel temperature. The material is p type in this temperature range. The results are interpreted on the basis of small-polaron hopping involving charge carriers in one or more sets of transport levels.

Introduction

The electrical properties of MnO have been repeatedly studied (1-21); however, in a large number of cases, the investigations were carried out on polycrystalline or single-crystal Li-doped samples. As is by now well established, data obtained on this basis are of limited utility because they are not representative of the undoped material. The results are at variance with each other and with findings on undoped MnO.

Investigations on single crystals of pure MnO have been less numerous: three prior sets (9, 14, 19) of measurements by different groups of investigators in the temperature range 300-650K yielded resistivities ρ and resistivity activation energies ϵ_ρ that were reasonably concordant (see Fig. 1). On the other hand, the reported Seebeck coefficients α vary widely (see Fig. 2). This situation is puzzling for several reasons: The results of Kleinpenning (19), and the results of Hed and Tannhauser (9), when extrapolated linearly into the temperature range $T = 300-600$ K, yield activation energies $\epsilon_{\alpha_r} = 2.303k [d\alpha_r/d(1/T)]$ which exceed the resistivity activation energies ϵ_ρ

$= 2.303k [d \log \rho/d (1/T)]$. Here $\alpha_r \equiv \alpha/2.303(k/e)$ is the reduced Seebeck coefficient, k is Boltzmann's constant, and $-e$ is the fundamental electronic charge. It is well established that the inequality $\epsilon_{\alpha_r} > \epsilon_\rho$ is incompatible with the ordinary model of a small-polaron material. As is shown below the generalization to a two-carrier small-polaron model is also incompatible with this result. It is possible to reconcile these observations with a model of a nearly intrinsic semiconductor, but only under the assumption that the two sets of charge carriers are itinerant (22). If the latter assumption were adopted the $Mn^{2+}3d^5$ electronic configuration should render MnO metallic.

The results quoted by Ksendzov (14) and by Joshi (21) lead to concordant values $\epsilon_{\alpha_r} < \epsilon_\rho$, that are compatible with a small-polaron model; however, the absolute values of α differ significantly. Furthermore, the charge carrier mobilities calculated from the difference $\epsilon_\rho - \epsilon_{\alpha_r}$ are considerably at variance with those determined by other investigators, based on Hall coefficient measurements (10, 13).

For the above reasons it was deemed

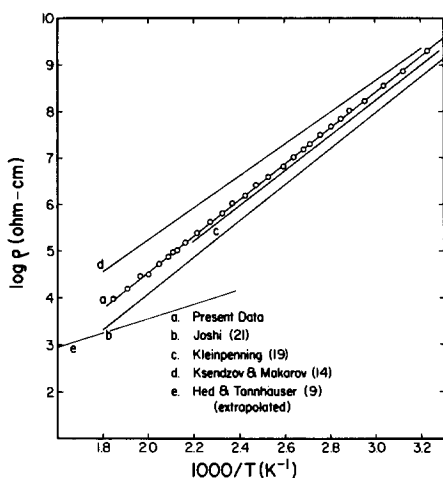


FIG. 1. Log specific resistivity against $1/T$ for annealed MnO single crystals.

desirable to initiate yet another study of the resistivity and Seebeck coefficient of undoped MnO single crystals. Considerable care was taken to achieve precise control over the sample stoichiometry, and to work with circuits that could adequately handle the large sample impedances in the low-temperature range of the measurements.

Experimental

Single crystals of MnO were prepared by use of a skull melter, whose operation is described elsewhere (20). The molten mass was kept at elevated temperatures for long periods of time to boil off impurities. Although the entire process was carried out in a buffered CO/CO_2 atmosphere, crystals obtained on cooling contained Mn_3O_4 inclusions, as detected both by X-ray diffraction and by optical microscopy with polarized light. Accordingly, a thin sample specimen was cut from a single-crystal portion of the boule, and annealed in a CO_2 atmosphere ($\log f_{\text{O}_2} = -12$) at 1200°C for 96 hr and then quenched. Reexamination showed that the Mn_3O_4 inclusions were totally eliminated in this process. The specimen was then cleaned ultrasonically with isopropyl alco-

hol, acetone, and water. Silver paint electrodes were applied; they were found to provide low-noise, ohmic contacts.

The resistivity measurements were carried out on three randomly selected samples from the bulk, in the temperature range 293–520 K. Copper–constantan thermocouples were used for temperature measurements. The resistance of the sample was directly measured with a Keithley 602 electrometer. To ascertain the reproducibility, several sets of data were taken. As an additional check, a four-probe resistivity measurement was carried out on one of the samples. The data were found to lie within 1% of the average resistivity plot shown in Fig. 1.

The Seebeck coefficient measurements were carried out using a specially designed, high-input impedance ($\sim 10^{14}$ ohm) circuit, in the temperature range 310–550 K. The thermal emf and the temperature difference across the sample were measured using copper leads, and copper–constantan thermocouples imbedded in small slots at each

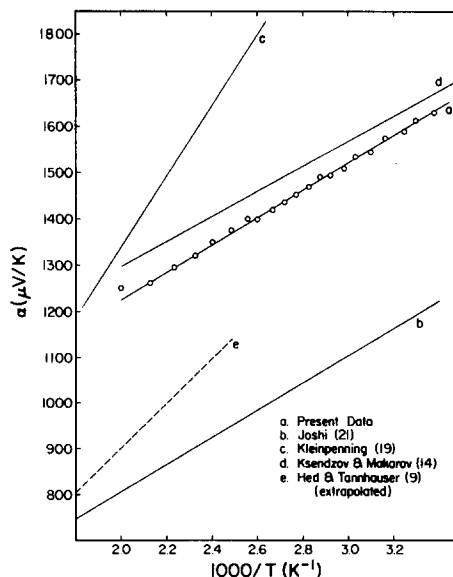


FIG. 2. Seebeck coefficient against $1/T$ for annealed MnO single crystals. Curve (d) taken from Ref. (18).

end of the sample. An additional thermocouple was used to record the average sample temperature. Measurements were carried out on four different samples and repeated three times to check on the reproducibility. The results were found to be in excellent agreement.

Results

The resistivity measurements are entered in Fig. 1 as a plot of $\log \rho$ vs $1/T$. Inspection shows that the present measurements, as well as the resistivity activation energy $\epsilon_p = 0.74$ eV, agree quite well with the measurements reported for undoped single crystals by all prior investigators (7, 14, 19, 21) for this temperature range. The present Seebeck coefficient measurements depicted in Fig. 2 lie fairly close to and run roughly parallel to those of Ksendzov (18); the computed activation energy, $\epsilon_\alpha = 0.30$ eV, also agrees well with that reported by Joshi (21), though the present α values are nearly 0.5 mV/deg higher than those in Ref. (21).

Discussion

The present measurements (as well as those in Refs. (7, 18, 21)) show that $\epsilon_\alpha < \epsilon_p$; hence, they should be amenable to an analysis based on the small-polaron transport model (8-10). On the assumption that only one set of carriers is involved in charge transport, that in the range of measurements kT is small compared to ϵ_g (the energy separation between the transport levels and the donor levels), and that Mn^{2+} is encountered in the high-spin configuration $\Delta_e > kT$, where Δ_e is the exchange energy, one finds that (23, 24)

$$\log \rho = \log n - \log \left(\frac{n_2}{n_0 - 1} \right) - \log \gamma_3 - \log u_0(T) + \frac{\epsilon_g + \epsilon_u}{2.303kT} \quad (1)$$

and

$$\alpha_r = \frac{\alpha}{2.303(k/e)} = - \log \frac{n_2}{n_0 - 1} + \log 2\gamma + \frac{\epsilon_g}{2.303kT} \quad (2)$$

Here $n = 4.62 \times 10^{22} \text{ cm}^{-3}$ is the density of cation sites in MnO; n_2 and n_0 are the densities of acceptor and compensating sites, $\gamma_3 = 1$ and $\gamma = 5.5$ are degeneracy factors computed under assumption stated in Ref. (24), and the small-polaron hole mobility is specified as $u = u_0 e^{-\epsilon_u/kT}$, where $u_0(T)$ is a weakly temperature-dependent function specified in Refs. (23) or (25, 26). If the variation of u_0 with temperature is ignored, the difference in slopes of the straight line plots shown in Figs. 1 and 2 may be used to compute the mobility activation energy as $\epsilon_u = 0.44$ eV for holes.

It may also be shown that (24)

$$\log \rho \approx \alpha_r - \log (2ne) - \log u. \quad (3)$$

Inserting appropriate values in Eq. (3), one obtains an activation energy for mobility of 0.45 eV. A plot of $\log u$ vs $1/T$, as determined from Eq. (3), is exhibited in Fig. 3. It is seen that mobilities fall in the range 1.8×10^{-5} to $1.7 \times 10^{-2} \text{ cm}^2\text{V-sec}$ for the temperature interval 230-500 K; these are compatible with values associated with small-polaron materials.

While a one-carrier model fits the above data, it should be recognized that a two-carrier small-polaron model has also been invoked for the interpretation of the electrical characteristics of MnO (7, 10, 14, 19). In an extension of the work by Kuipers and Brabers (22) it is readily shown that for the strictly intrinsic case

$$\log \rho_{in} = - \log \left[N_0 e u_0 (1 + b) \left(\frac{g_1}{g_2} \right)^{1/2} \right] + \frac{\epsilon_u + \Delta}{(2.303k) \cdot T} \quad (4)$$

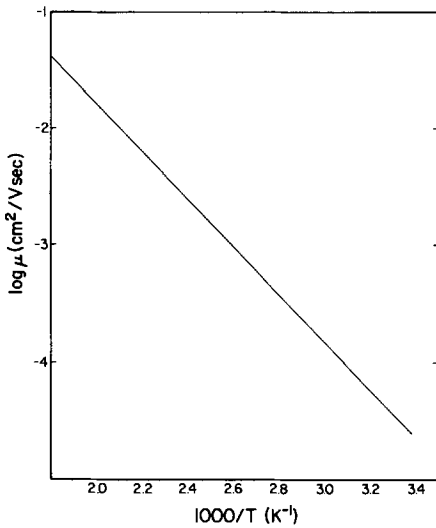


FIG. 3. Calculated log mobility against $1/T$ from the present data.

$$\alpha_r = \frac{\alpha_{ln}}{2.303k/e} = -\frac{1}{2} \log(g_1 g_2) + \left(\frac{1-b}{1+b}\right) \frac{\Delta}{2.303k} \frac{1}{T} \quad (5)$$

Here N_0 is the density of cationic sites, g_1 and g_2 are degeneracy factors for electrons and holes, $b \equiv u_n/u_p < 1$ is the ratio of electron to hole mobility, and 2Δ is the energy difference in the two sets of levels associated with charge carrier transport. In conformity with the fact that MnO is p type, u_0 quoted in Eq. (4) pertains to holes; the electron mobility is attended to by the factor $(1+b)$. Since b is the ratio of mobilities we have ignored the temperature variation of b , which is permissible if the difference between electron and hole mobility activation energies is either small or large relative to kT . If S_ρ and S_{α_r} are the slopes of the plots of $\log \rho_{ln}$ vs $1/T$ and of α_r vs. $1/T$ respectively, then their ratio is given by

$$\frac{S_{\alpha_r}}{S_\rho} = \left(\frac{1-b}{1+b}\right) \left(\frac{1}{1+\epsilon_u/\Delta}\right) < 1. \quad (6)$$

Equation (6) shows that for the elementary two-carrier model described above S_{α_r} cannot exceed S_ρ ; thus, such a model cannot be invoked to explain the results of Refs. (9) and (19). To interpret the present data for which $S_{\alpha_r}/S_\rho = 0.399$ an estimate of Δ is required. If 2Δ is considered to be given by the crystal field splitting effects, one finds (27) $\Delta = 0.5$ eV; this would lead to a mobility activation energy in Eq. (4) of $\epsilon_u = 0.24$ eV, and would yield $b = 0.26$ in Eq. (5). While such values are physically plausible, the intercept of the α_r vs $1/T$ plot, $I_\alpha = 3.17$, leads to an unreasonably small value of the product $g_1 g_2$; it is therefore doubtful if the two-band model should be applied to the present case. For this reason we adopt the one-carrier analysis associated with Eqs. (1)–(3).

It should be noted that the mobility values quoted earlier bracket those cited by various authors (9, 11, 13) on the basis of Hall measurements. However, one must keep in mind the repeated warnings by Emin and collaborators (28), that Hall coefficient data for small-polaron materials cannot be interpreted in the same manner as for itinerant semiconductors or for metals. For this reason it seems preferable to introduce the results of Fig. 3 into the expression $\sigma = neu$ for the calculation of charge carrier densities.

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