

Defect structure of acceptor-doped calcium titanate at elevated temperatures

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The defect structure of acceptor (Al or Cr)-doped polycrystalline calcium titanate was investigated by measuring the oxygen partial pressure dependence (at 10^0 to 10^{-18} atm) of the electrical conductivity at 1000 and 1050° C. The observed electrical conductivity data were proportional to $P_{O_2}^{-1/4}$ for the oxygen pressure range $< 10^{-10}$ atm and proportional to $P_{O_2}^{+1/4}$ for the oxygen pressure range $> 10^{-7}$ atm. The conductivity values were observed to increase with the acceptor concentration in the p-type region with the shift in the conductivity minima towards lower oxygen partial pressure. The absolute value of the electrical conductivity in the acceptor-doped samples were lower in the n-type region compared to the values in the undoped $CaTiO_3$. Aluminium and chromium were found to be equally effective in acting as acceptor impurities in $CaTiO_3$. The defect chemistry of $CaTiO_3$ is dominated by the added acceptor impurities for the entire oxygen partial pressure range used in this investigation.

1. Introduction

While the defect structures of $BaTiO_3$ and $SrTiO_3$ have been studied in considerable detail [1-11], $CaTiO_3$ has received comparatively little attention. George and Grace [12, 13] examined the electrical conductivity, Seebeck coefficient and diffusion of point defects in single crystal $CaTiO_3$ in water-hydrogen atmospheres in the temperature range 1100 to 1300° C. The present authors [14, 15] have studied the defect structure of undoped and lanthanum-added polycrystalline $CaTiO_3$ by means of equilibrium electrical conductivity in the oxygen partial pressure, P_{O_2} , range 10^0 to 10^{-22} atm and temperature range 800 to 1100° C. The p-type conductivity observed in the P_{O_2} range greater than 10^{-4} atm in undoped $CaTiO_3$ [14] results from a stoichiometric excess of oxygen which occupies the impurity-related oxygen vacancies. Similar results were observed by Balachandran and Eror [9] in undoped $SrTiO_3$. For the case of undoped $SrTiO_3$ prepared by the same technique as the one used here, the unknown acceptor impurity concentration has been estimated to be about 170 ppm [9]. Chan and Smyth [5] pointed out that acceptor impurities, such as Na^+ , K^+ , Fe^{2+} , Fe^{3+} , Mg^{2+} and Al^{3+} , are much more likely to be present than

donor impurities, such as La^{3+} and other rare earths or Th^{4+} , Nb^{5+} , Ta^{5+} , W^{6+} etc., because of their greater natural abundances. The effect of known amounts of acceptor impurities on the equilibrium electrical conductivity in $CaTiO_3$ have not been reported in the literature.

In the present study, the defect structure of calcium titanate doped with aluminium or chromium is investigated by measuring the electrical conductivity at 1000 to 1050° C while in equilibrium with the oxygen partial pressure of the surrounding atmosphere. The amounts of Al or Cr selected are 0.25, 0.35, 0.55 and 0.7 at% in the general formula $CaA_xTi_{1-x}O_3$ where A represents the added acceptor element.

2. Experimental procedure

The samples employed in this investigation were prepared by a liquid mix technique [9-11, 13, 16]. The required amounts of calcium carbonate (Mallinckrodt Chemical Works), tetraisopropyl titanate solution (Dupont Co., Tyzor) and aluminium nitrate (Johnson Mathey Chemicals Ltd.) or chromium nitrate (Fisher Scientific Co.) were dissolved in an ethylene glycol-citric acid solution. There was no evidence of any precipitation

in the solutions as they were evaporated to a rigid, transparent, uniformly coloured polymeric glass. The glass retains homogeneity on an atomic scale and was calcined at 900°C: there was no evidence of a second phase in the calcined samples. The calcined powder samples were pressed into thin circular discs at 275 MPa and sintered in air at 1350°C for 12 h. Electrical conductivity specimens were cut from the sintered discs using an airbrasive unit. The specimens were wrapped with four 0.025 cm platinum wires, as described in the literature [17, 18]. Small notches were cut in the edges of the sample to aid in holding the platinum wires in place. A conventional four-probe direct current technique was employed for all electrical conductivity measurements and the experimental details have been described previously [9, 19, 20].

3. Results and discussion

The measured electrical conductivities of Al or Cr doped calcium titanate as a function of P_{O_2} at 1000 and 1050°C are given in Figs 1 and 2, respectively. The data obtained in our previous investigation [14] of undoped $CaTiO_3$ are also shown in Figs 1 and 2. For the acceptor doped samples, no region with $-1/6$ th dependence of conductivity on oxygen pressure was observed. The results show that the electrical conductivities

of the samples are proportional to $P_{O_2}^{-1/4}$ for the oxygen pressure range $< 10^{-10}$ atm and proportional to $P_{O_2}^{+1/4}$ for $P_{O_2} > 10^{-7}$ atm. Increases in the concentrations of Al or Cr give rise to higher conductivity values in the p-type region and lower values in the n-type region compared with the values in the undoped $CaTiO_3$. This shifts the n-p transition to lower P_{O_2} values as the acceptor concentration is increased. For the sample with 0.7 at% Al or Cr, the conductivity minima is somewhat flattened and the P_{O_2} -independent conductivity observed in these samples are tentatively identified as oxygen vacancy conduction.

3.1. Region I ($P_{O_2} < 10^{-10}$ atm)

The electrical conductivity in the region of $P_{O_2} < 10^{-10}$ atm increases with decreasing oxygen partial pressure, indicative of n-type, or metal-excess, conductivity. The $\log \sigma$ against $\log P_{O_2}$ plot is linear for as many as seven decades of oxygen partial pressure at a given temperature. This extensive region of linearity affords the opportunity to determine the defect model responsible for the n-type conduction in this region. A slope of approximately $-1/4$ is found for the $\log \sigma$ against $\log P_{O_2}$ data (see Figs 1 and 2). The present authors [14] have observed a range of $P_{O_2}^{-1/4}$ dependence for conductivity in the

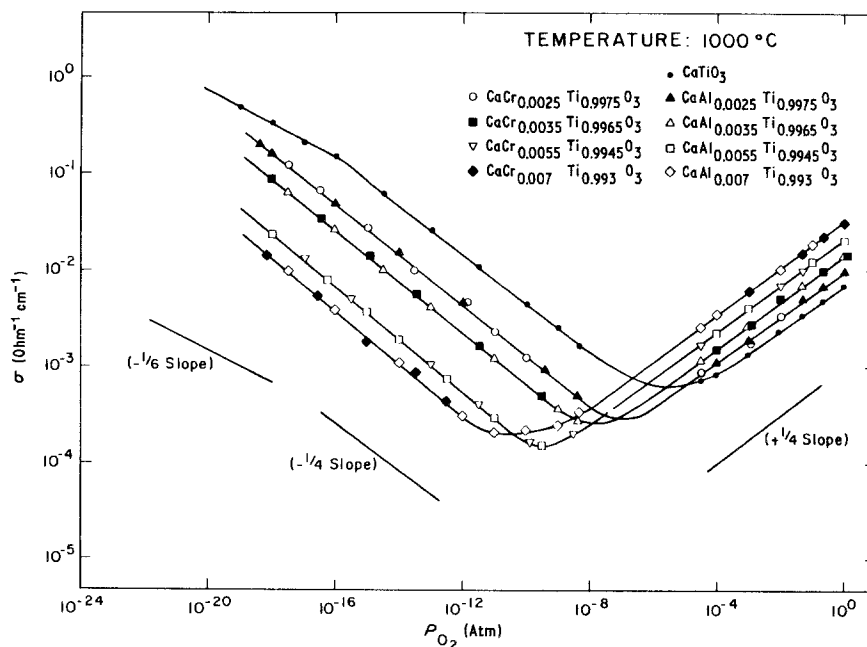


Figure 1 Electrical conductivity in acceptor (Al or Cr)-doped calcium titanate as a function of oxygen partial pressure at 1000°C.

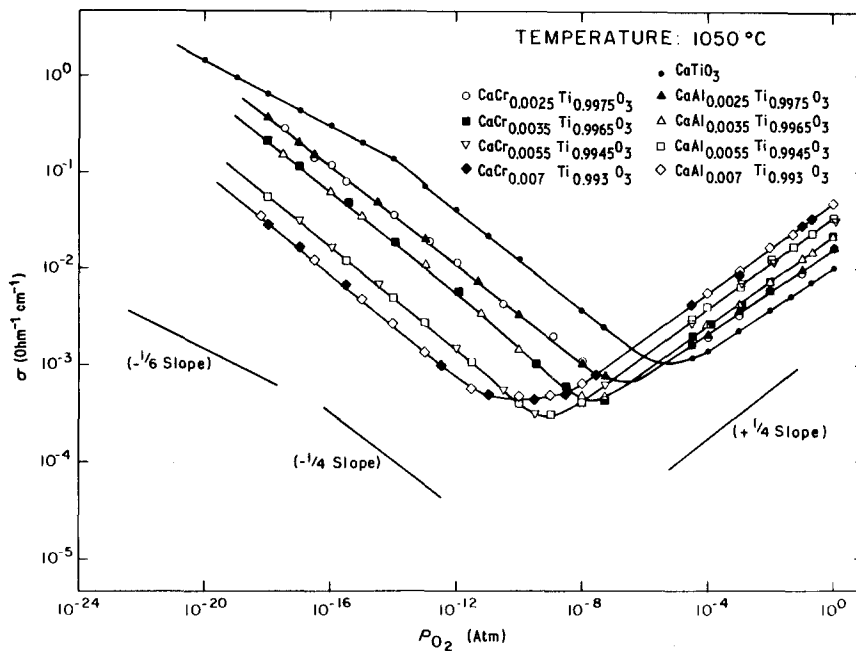


Figure 2 Electrical conductivity in acceptor (Al or Cr)-doped calcium titanate as a function of oxygen partial pressure at 1050°C.

oxygen-deficient region below the p-n transition in undoped CaTiO_3 due to the presence of accidental acceptor impurities. It is seen in Figs 1 and 2 that the absolute values of the measured conductivity in the samples with equal concentration of Al or Cr is the same, indicating that aluminium and chromium are equally effective as acceptors in CaTiO_3 . Similar behaviour was observed in acceptor doped $\alpha\text{-Nb}_2\text{O}_5$ [21].

A Kroger-Vink diagram [22] is a useful representation to consider when discussing the electrical conductivity in ternary oxides of the type ABO_3 with added impurities. We will, for the purpose of illustration, consider Schottky-Wagner disorder to describe the non-stoichiometry. Fig. 3 illustrates the variation of defect concentrations as a function of oxygen partial pressure for the case of fully ionized atomic defects, elec-

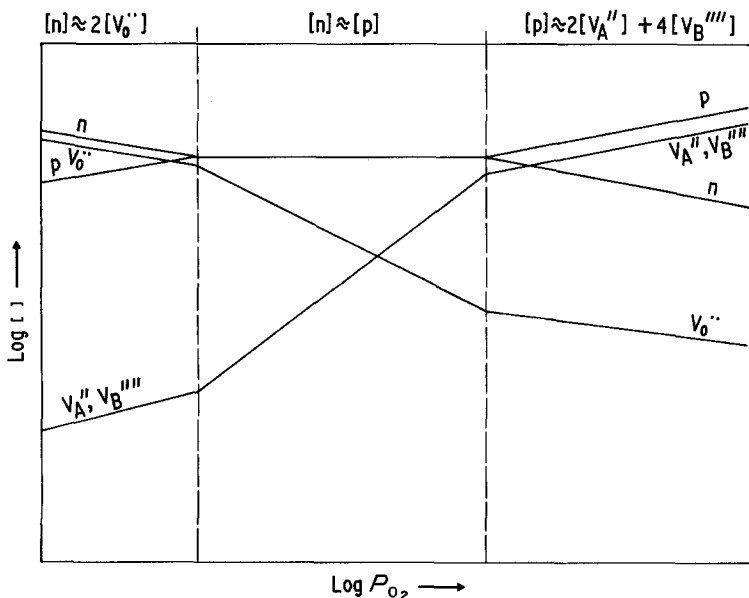


Figure 3 Defect concentrations against the oxygen pressure in the ternary oxide of the type ABO_3 with Schottky-Wagner disorder.

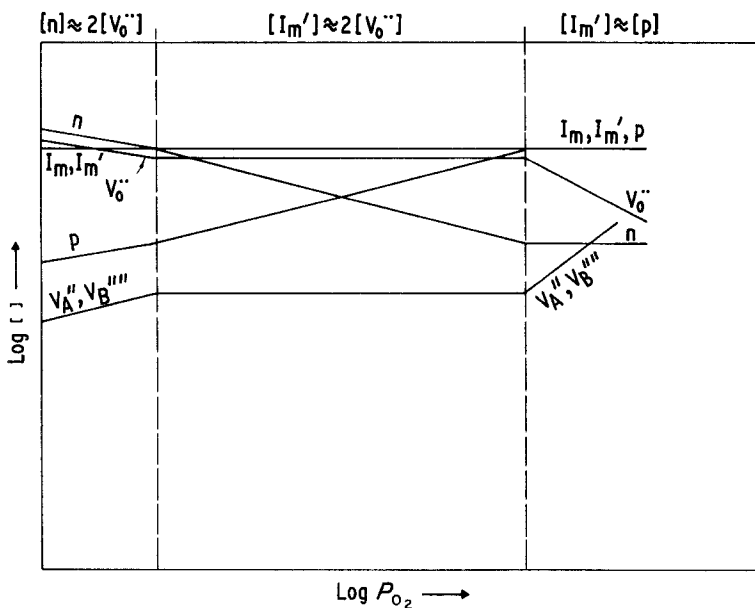


Figure 4 Logarithm of the defect concentration for the ternary oxide ABO_3 , with a fully ionized acceptor impurity, I_m , and Schottky–Wagner disorder as a function of logarithm of oxygen pressure.

trons (n), and electron holes (p) in a ternary oxide ABO_3 , where both A and B are site vacancies. The familiar $[n] \propto P_{O_2}^{-1/6}$ in the region with the charge neutrality condition $[n] \approx 2[V_O'']$ where V_O'' is a doubly-charged oxygen vacancy is illustrated in Fig. 3. In Fig. 4 an acceptor impurity is added to the oxide that is always fully ionized, I_m' . Note in Fig. 4 that for sufficient departures from stoichiometry it may be possible for the electrical conductivity to be controlled by $[n] \approx 2[V_O'']$ and to thereby mask the effect of the added acceptor impurity. The two major points to be derived from Fig. 4 are that when an acceptor impurity is added, the electronic n to p transition shifts to lower oxygen partial pressures, while the metal excess to metal deficit transition shifts to higher oxygen partial pressures.

In Fig. 4 there is a region with the charge neutrality condition $[I_m'] \approx 2[V_O'']$ in which the electron concentration varies as $P_{O_2}^{-1/4}$ and the electron hole concentration increases as a $+1/4$ th power of the oxygen partial pressure. In this region, for certain values of P_{O_2} , the electron concentration is greater than the electron hole concentration and hence the conductivity is n -type with a $-1/4$ th dependence on P_{O_2} . As the P_{O_2} value increases, the electron hole concentration becomes greater than an electron concentration and the material becomes p -type with a $+1/4$ th dependence for conductivity on oxygen partial pressure. When the P_{O_2} value is increased further, the electron hole concentration becomes equal to the acceptor concentration, which is con-

stant, and hence the conductivity is independent of P_{O_2} , with the charge neutrality condition $[I_m'] \approx [p]$ as shown in Fig. 4. The observation of P_{O_2} independent electrical conductivity with the charge neutrality equation, $[I_m'] \approx [p]$ depends on the amount of acceptor impurity added to the oxide and P_{O_2} values used in the investigation.

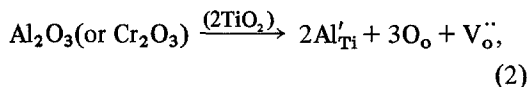
It should be pointed out here that Figs 3 and 4 represent the variation of defect concentration for the general case of a ternary oxide ABO_3 in which vacancies on both A and B sites are considered to be present simultaneously. The presence of B-site vacancies in perovskites has been reported for lanthana-substituted $PbTiO_3$ by Hennings and Rosenstein [23], and for lanthanum manganite by Tofield and Scott [24]. Rauser and Kemmler–Sack [25] have reported the ordered perovskites with B-site vacancies, for a new series of composition $Ba_2^{2+}B^{3+}U_{5/6}^{6+}\square_{1/6}O_6$ and where \square is a vacancy for $B^{3+} = Sm$ to Lu , Sc , and Y . The existence of vacancies on both A and B sites in $CaTiO_3$ or in the structural analogues $BaTiO_3$ and $SrTiO_3$, are not reported in the literature.

The observed slope of approximately $-1/4$ in this region must, therefore, be due to the added acceptor impurities. The condition of charge neutrality in this region is

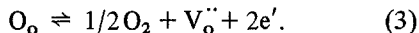
$$[I_m'] \approx 2[V_O'']_{\text{ext}} = \text{constant}, \quad (1)$$

where I_m' represent Al'_{Ti} or Cr'_{Ti} and $[V_O'']_{\text{ext}}$ is the extrinsic oxygen vacancy concentration controlled by the acceptor impurity content as shown

in



where it is assumed that the oxides of Al or Cr replace 2TiO_2 in the calcium titanate lattice. One should also consider the removal of an oxygen atom from the normal lattice site into the gas phase leaving a doubly-ionized oxygen vacancy and two electrons available for conduction. This reduction reaction is given in



The mass-action expression for Reaction 3 is

$$[\text{V}_\text{o}''] [\text{n}]^2 \approx K_3 P_{\text{O}_2}^{-1/2} = K_3' P_{\text{O}_2}^{-1/2} \exp \left[-\frac{\Delta H_f}{RT} \right], \quad (4)$$

where ΔH_f is the standard enthalpy of Reaction 3.

If the extrinsic V_o'' concentration fixed by the acceptor impurities is larger than the V_o'' from the reduction reaction, Equation 3, then the charge neutrality condition, $[\text{I}'_\text{m}] \approx 2[\text{V}_\text{o}'']_{\text{ext}}$, is valid in this region. Substituting the charge neutrality condition, Equation 1 into Equation 4 yields

$$[\text{n}] \approx \left(\frac{2K_3'}{[\text{I}'_\text{m}]} \right)^{1/2} P_{\text{O}_2}^{-1/4} \exp \left[-\frac{\Delta H_f}{2RT} \right], \quad (5)$$

and the electrical conductivity, σ , is given by

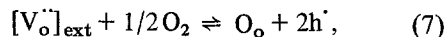
$$\sigma = \left(\frac{2K_3'}{[\text{I}'_\text{m}]} \right)^{1/2} e\mu P_{\text{O}_2}^{-1/4} \exp \left[-\frac{\Delta H_f}{2RT} \right], \quad (6)$$

where e is the electronic charge and μ is the mobility of electrons. If one assumes that the mobility is independent of the change in the concentration of oxygen vacancies, a plot of $\log \sigma$ against $\log P_{\text{O}_2}$ should result in a straight line with a slope of $-1/4$. The data in Figs 1 and 2 are in excellent agreement with the predicted $-1/4$ th dependence of conductivity on P_{O_2} in the oxygen partial pressure range $< 10^{-10}$ atm. The added acceptor impurities decrease the concentration of free electrons available for conduction and therefore, the measured conductivity is lower than that observed in the undoped sample for the same oxygen partial pressure value in the n-type region.

3.2. Region II: ($P_{\text{O}_2} > 10^{-7}$ atm)

The electrical conductivity in the region of P_{O_2} greater than 10^{-7} atm increases with oxygen partial pressure, indicative of p-type or oxygen

excess, conductivity. The region of linearity in the p-type region increases in width with acceptor concentration. A slope of about $+1/4$ is found for the $\log \sigma$ against $\log P_{\text{O}_2}$ data (see Figs 1 and 2). The addition of an acceptor impurity makes available an energetically favourable mechanism for the addition of excess oxygen into a perfect calcium titanate perovskite lattice. It is shown in alkaline earth titanates [3, 5, 7, 9, 14] that the p-type conductivity arises from the incorporation of oxygen into the impurity-related oxygen vacancies where the reaction is



where $[\text{p}] \equiv h'$. The mass-action expression for Reaction 7 is

$$\frac{[\text{p}]^2}{[\text{V}_\text{o}'']_{\text{ext}}} = K_7 P_{\text{O}_2}^{1/2} = K_7' P_{\text{O}_2}^{1/2} \exp \left[-\frac{\Delta H_p}{RT} \right], \quad (8)$$

where ΔH_p is the standard enthalpy change for the reaction represented by Equation 7. The charge neutrality condition in this region would still be represented by Equation 1, i.e.,

$$[\text{I}'_\text{m}] \approx 2[\text{V}_\text{o}'']_{\text{ext}} = \text{constant}.$$

Combination of Equations 1 and 8 gives

$$[\text{p}] = \left(\frac{K_7' [\text{I}'_\text{m}]}{2} \right)^{1/2} P_{\text{O}_2}^{1/4} \exp \left[-\frac{\Delta H_p}{2RT} \right]. \quad (9)$$

This gives

$$\sigma \propto P_{\text{O}_2}^{+1/4} \quad (10)$$

as long as only a minor fraction of the impurity-related oxygen vacancies is filled. The observed slope of $\sim 1/4$ (see Figs 1 and 2) in the p-type region agrees well with the above predicted value. Under no conditions to date has the oxygen addition been sufficient to consume all of the impurity-related V_o'' in the samples [8]. By the above model of incorporating excess oxygen into impurity-related V_o'' , a stoichiometric excess of oxygen (more than enough oxygen to satisfy the maximum oxidation states of the cationic content) is achieved without the need for creating a crystallographic excess (more oxygen than the number of available lattice sites).

The onset of the p-type conductivity depends on the amount of the acceptor impurity added to the sample. With an increase in the acceptor concentration, the impurity-related oxygen vacancy concentration, $[\text{V}_\text{o}'']_{\text{ext}}$, increases. This means

more oxygen atoms can be incorporated into these vacancies leading to an increased concentration of electron holes. This gives rise to the observed increase in the conductivity values with added acceptor impurities in the p-type region. This observation, and the fact that the absolute value of the conductivity in the n-type region decreases with increasing acceptor concentration, shifts the conductivity minima to lower P_{O_2} as the amount of Al or Cr added to calcium titanate is increased. The conductivity minima in the case of 0.55 at% Al or Cr doped samples are shifted by about four orders of magnitude to lower P_{O_2} compared to the undoped $CaTiO_3$ sample (see Figs 1 and 2).

For the sample with 0.7 at% Al or Cr, the conductivity minima are slightly flattened. Similar behaviour has been observed recently by Chan *et al.* [8, 11] in $BaTiO_3$ and $SrTiO_3$ and attributed to oxygen vacancy conduction (ionic conduction). Ionic contribution to the conductivity of perovskite structure oxides with large amounts of acceptor impurities has been reported in the literature [26]. In the case of undoped $BaTiO_3$, the ionic contribution near the conductivity minima is about 20% of total conductivity at 750°C [8]. We postulate that the observation of nearly P_{O_2} -independent conductivity near the conductivity minima in 0.7 at% Al or Cr doped samples represents oxygen vacancy condition. This P_{O_2} -independent conductivity is presumably due to the P_{O_2} -independent concentration of extrinsic $V_O^{\bullet\bullet}$ present in the acceptor doped samples. Measurement of the ionic transference number and the effect on the ionic conductivity of the added acceptor impurities are currently under investigation.

4. Conclusions

The measured electrical conductivity in Al or Cr doped $CaTiO_3$ was proportional to about $-1/4$ th power of P_{O_2} for the oxygen partial pressure range $< 10^{-10}$ atm. The defect chemistry of $CaTiO_3$ is dominated by the added acceptor impurities and their related oxygen vacancies, Equation 1, for the entire P_{O_2} range used in this work. The observed values of the electrical conductivity in the acceptor doped samples is less than that of the undoped samples in the n-type region and the values decrease with increase in concentration of Al or Cr. The conductivity values were observed to be the same in samples with Al or Cr of same concentration and this indicated

that both these elements are equally effective as acceptor impurities.

For $P_{O_2} > 10^{-7}$ atm the electrical conductivity was found to be proportional to $P_{O_2}^{+1/4}$. The observed p-type conductivity results from a stoichiometric excess of oxygen which occupies the impurity-related oxygen vacancies, Equation 6. A stoichiometric excess of oxygen is achieved even while not all of the available oxygen sites are occupied. The measured electrical conductivity values increase with acceptor concentration in the p-type region and the conductivity minima shifts to lower oxygen partial pressure. The samples with 0.7 at% acceptor concentration showed nearly a P_{O_2} -independent conductivity near the conductivity minima and this is tentatively identified as oxygen vacancy conduction.

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