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Transport Phenomena in Pure and Doped Magnesium Oxide

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Ac electrical conductivity measurements have been made on polycrystalline samples of various compositions in the MgO-NiO system. Four activation energies have been obtained with pure MgO: 5.2, 2.7, 3.5, and 0.92 eV. These seem to be the activation energies, respectively, for intrinsic O^- conductivity, extrinsic O^- conductivity, intrinsic Mg^{++} conductivity, and extrinsic Mg^{++} conductivity. Introduction of NiO into the specimens increases the conductivity and decreases the activation energy. The conductivity of the polycrystalline MgO specimens used in this study is larger than literature data for MgO single crystals. This difference results from the large number of grain boundaries present in polycrystals.

INTRODUCTION

IN comparison to the extensive measurements of diffusion and electrical conductivity of alkali halides, the ionic oxides have been more or less neglected. This has been partially caused by the unavailability until recently of such oxides of reasonable purity. Using activation energies as guides, we have attempted to determine the current carriers for the conductivity process in magnesium oxide. Although contradictory results exist in the literature, we have been able to take many of the earlier data and obtain a consistent picture based upon ionic conduction not only for magnesium oxide but for the ionic oxides in general. References to previous work are included at appropriate points in the results and discussion sections.

It is important to realize that all oxides are not similar in their properties. Oxides may be divided into two groups on the basis of density of oxide in comparison with density of metal. For those oxides with density greater than that of the metal, the distance between metal ions in the oxide is less than that in the metal. Examples of such oxides are the truly ionic oxides—the alkali-metal oxides, aluminum oxide, and the alkaline-earth oxides. (Magnesium oxide is a member of this group.) The other group of oxides, with oxide density less than that of the metal, includes the transition-metal oxides such as pure NiO, FeO, CoO, and MnO, in which electronic conductivity predominates. Such oxides are certainly not examples of truly ionic materials and are not discussed in this paper. Conclusions based on either set of compounds must be carefully

checked for validity before being applied to the other set of compounds where the type of bonding differs.

The system MgO-NiO bridges the gap between the ionic oxide MgO and the transition-metal oxide NiO. We have selected this system for the initial step of a more general program on diffusion and conduction in mixed oxides. The advantages of MgO-NiO for a conductivity study are: (1) Both are cubic oxides. (2) Complete solid solubility exists in this system. (3) Both oxides possess relatively good stability against decomposition in the temperature range of interest (900° to 1500°C). (4) Replacement of Mg^{++} by Ni^{++} in the oxide lattice does not introduce a strain in the lattice since the Goldschmidt radii are identical (0.78 Å). The system MgO-NiO is also particularly suitable for diffusion studies because of the difference in color of the oxides, Ni^{++} can be chemically analyzed with a lower limit in the microgram range, and stable isotopes can be utilized. The use of stable isotopes introduces no impurities as the result of radioactive decay. The electrical conductivity results will be reported in this paper. It is hoped that future studies of transport number and diffusion on samples of similar history will help to clarify the transport processes in this system. Although the primary emphasis has been on the system MgO-NiO, electrical conductivity measurements on one composition of the system CoO-MgO and on Al_2O_3 are also presented.

Since the activation energies for conductivity are found to be the same for single crystals and polycrystals of MgO, we feel that purity and uniformity of compo-

TABLE I. Typical analysis of MgO (in weight percent).

MgO assay	98.0%
Ignition loss	1.6%
Insoluble in concentrated HCl	0.09%
Water soluble	0.55%
Ammonium hydroxide precipitate	0.005%
SiO ₂	0.10%
Sulfur (as sulfate ion)	0.013%
Calcium	0.01%
Iron	0.03%
Chloride	Trace
Nitrate	None
Copper	Trace
Vanadium	Trace
Boron	Trace
Sodium	None
Titanium	None
Zinc	None
Manganese	None
Aluminum	None
Barium	None

sition are by far the most important factors to consider at present in the selection of conductivity and diffusion specimens. On this basis, the single crystals of these oxides that are readily available in fairly large quantities seem to be far less suitable materials for study than is generally appreciated. In order to clarify the transport phenomena, what is really needed at present are carefully conducted experiments both on the best available single crystals and also on the best available polycrystals.

EXPERIMENTAL PROCEDURE

The polycrystalline specimens used for this investigation were prepared in the following manner: The powders were mixed dry in a blender. No binder was used. Great care was necessary in this step to obtain adequate mixing since the powders tended to adhere to the glass sides of the blender.

The resulting mixed powder was placed in a double covering of thin rubber tubing both 1 in. in diam and then slowly pressed to 50 000 psi (in approximately 3 min) in a hydrostatic press. The pressure was slowly released (in approximately 3 min). The resulting compacts were cut with a jeweler's saw.

The specimens were fired in slowly flowing Linde argon in a Globar furnace equipped with a nonporous alumina tube. The specimens were placed in the center of powder, of the same composition as the compacts, held in a high-purity (Morganite Triangle RR) alumina boat. Spectrographic comparisons of the starting powder and of the finished specimens showed that there was no increase in the concentration of aluminum as a result of this procedure. To prevent thermal shock

of the specimens the furnace was heated and cooled slowly. The specimens were kept at 1300°C for approximately 60 h.

The fabrication of specimens into cylinders was completed by a final shaping process using special holders and rotating disks of abrasive paper (Adalox 120 E). The approximate dimensions of the specimens were 1 cm in diam and $\frac{1}{2}$ cm high. The bulk densities of pure MgO specimens prepared in this way were 3.3 to 3.4 g/cm³. (The theoretical density for MgO is 3.56 g/cm³.) The average grain size was approximately 5 μ .

The compacts tended to crack if exposed to moist air when reagent-grade MgO was used.¹ Therefore, low-activity electronic-grade magnesium oxide (produced by the Morton Chemical Company) was used. Except for a slightly higher content of SiO₂, this material was of comparable purity to reagent-grade MgO. The average particle size of this material before compaction and fabrication is in the range 0.05 to 0.10 μ . A typical analysis of the magnesium oxide powder (as supplied by the manufacturer) is presented in Table I. The NiO used was reagent-grade material obtained from the J. T. Baker Company. The analysis of the specific lot of NiO used (as supplied by the manufacturer) is presented in Table II.

Figure 1 shows the inert atmosphere furnace and Fig. 2 an enlargement of the upper end assembly of the furnace used for conductivity measurements. The heating element for this furnace is Pt-40%Rh alloy. The winding temperature is controlled to $\pm 3^\circ\text{C}$ by a Pt-5%Rh vs Pt-40%Rh thermocouple placed in a well inside the winding. All electrical leads are bare wire at the point where they pass through the nonporous rubber of the sealing gland to make a gas-tight seal possible. The alumina inserts for this furnace are nonporous, SiO₂-free material (Morganite Triangle RR).

The electrode holder (shown in Fig. 3) is supported on the top of a similar alumina tube in the center of the furnace. The electrode design is that developed by

TABLE II. Composition of the NiO used.

NiO assay	99.6%
Nitrogen compounds (as N)	0.002%
Chloride (Cl ⁻)	0.002%
Sulfate (SO ₄ ²⁻)	0.002%
Lead (Pb)	0.001%
Copper (Cu)	0.005%
Cobalt (Co)	0.003%
Iron (Fe)	0.005%
Zinc (Zn)	0.005%
Alkalies and alkaline earths (as sulfates)	0.12%

¹ M. O. Davies, H. H. Grimes, and C. E. May, J. Am. Ceram. Soc. 44, 63 (1961).

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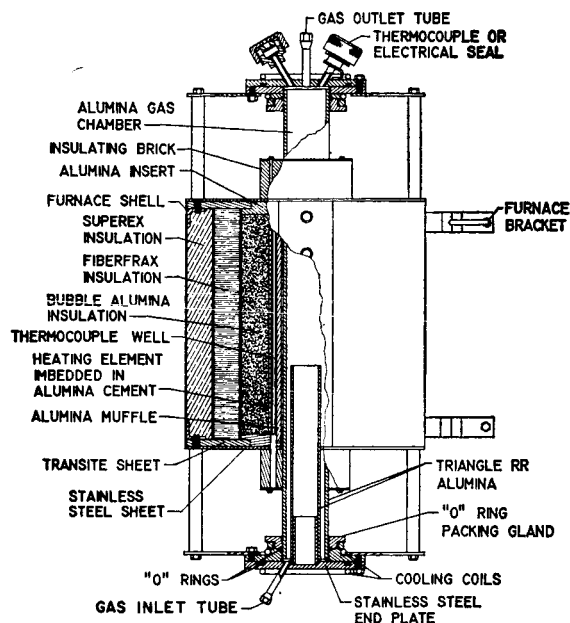


FIG. 1. Inert atmosphere furnace.

Northrup²; it permits one to obtain a good contact between specimen and electrode without introducing a resistance in parallel with that which is to be measured. The electrodes for these measurements (*a*, *b*, *c*, and *d*) are molybdenum clad with 0.01-in.-thick Pt-10%Rh alloy. The studs and nuts of this holder as well as the electrical leads (1 and 2) are solid Pt-10%Rh alloy. Three specimens (A, B, and C) of identical composition and known dimensions are used in the determination. With the arrangement described, one measures the resistance of Specimen B in parallel with the series combination of Specimens A and C.

Since Pt-Rh alloy is not reversible electrochemically to Mg^{++} nor to O^- in the absence of O_2 gas, it is necessary to use alternating current for the measurements.

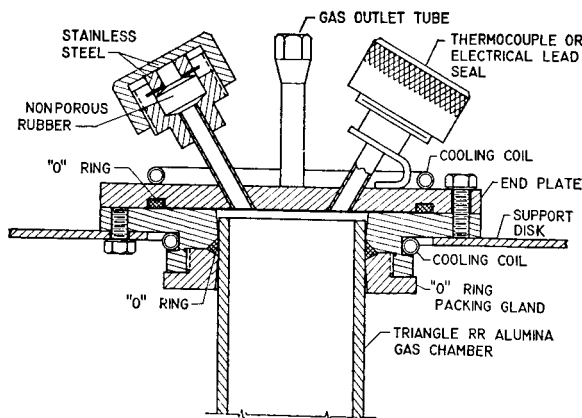
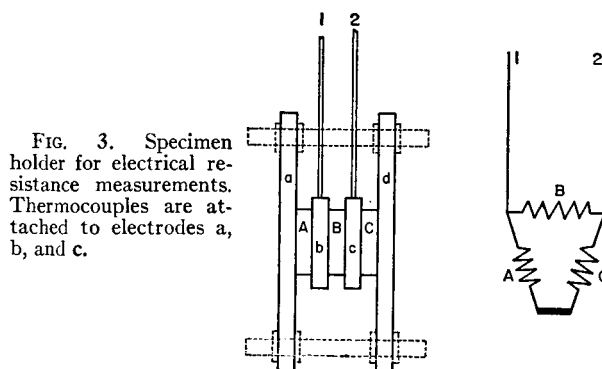


FIG. 2. Upper end assembly for inert atmosphere furnace.

FIG. 3. Specimen holder for electrical resistance measurements. Thermocouples are attached to electrodes *a*, *b*, and *c*.

The specimen was considered to have an equivalent circuit of parallel resistance and capacitance. A General Radio Type 1610-A capacitance bridge was used for the measurements at frequencies ranging from 0.1 to 100 kc/sec. The use of the guard circuit of this bridge is essential in obtaining meaningful measurements.

Flowing Linde welding grade argon (99.995% min.) was used as the atmosphere for most of the measurements and was held at approximately 3-psi gage pressure for most of the measurements. The composition of this argon as stated by the manufacturer is presented in Table III. Special regulators manufactured by the Harris-Calorific Company (Model AA 1200) were used to ensure that the gas introduced into the experimental system was of the same composition as that in the gas cylinder. There were no flexible connections in the gas line to the furnace. All gas lines to the furnace, plus the furnace chamber itself, were pressure checked before use to determine whether gas leaks existed in the system.

EXPERIMENTAL RESULTS

When the logarithm of electrical conductivity of an ionic solid is plotted vs the reciprocal of absolute temperature, one often finds two intersecting lines. The intersection is known as the knee of the curve. The slope of the higher-temperature portion is generally larger. The high- and low-temperature portions of such curves are also referred to as the intrinsic and extrinsic portions, respectively. Activation energies for ionic conductivity from the intrinsic range possess a contribution

TABLE III. Linde argon specifications.

Argon	99.995% min
Oxygen	less than 10 ppm
Nitrogen	less than 20 ppm
Hydrogen	less than 1 ppm
Carbon-bearing gases (hydrocarbons, CO ₂ , etc.)	less than 5 ppm
Water	less than 6 ppm
	(i.e., $\frac{2 \text{ grains}}{1000 \text{ cu ft}} \text{ max}$)

² E. F. Northrup, Met. Chem. Eng. 12, 125 (1914).

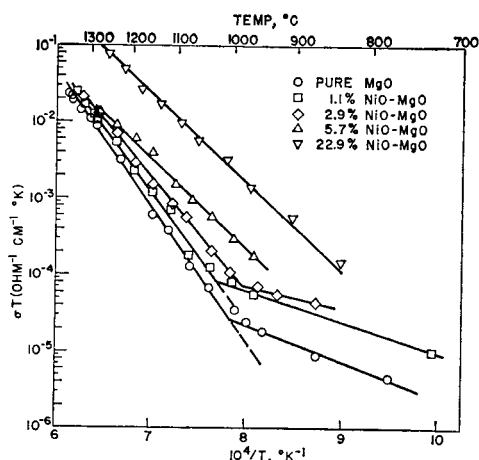


FIG. 4. Conductivity data for the MgO-NiO system.

from the energy of formation of the defect responsible for conduction as well as the contribution from the energy of migration. In the extrinsic range there is only the contribution from the energy of migration; the defect concentration is determined by the concentration and type of impurities present. To obtain the activation energy for conductivity, one really should plot logarithm of the product of electrical conductivity and absolute temperature vs reciprocal absolute temperature to take into account the temperature dependence of the pre-exponential term of the conductivity equation, as has been pointed out by Lidiard.³

The data for the electrical conductivity of various compositions in the MgO-NiO system are presented in Fig. 4. The compositions are in mole percent. It can be seen that the addition of NiO leads to increases of conductivity. The high-temperature slope (i.e., the slope above the knee) decreases with increases of NiO through 2.9% NiO. Not only are the slopes for the 5.7% and 22.9% specimens the same, but also there is no indication of a knee in the conductivity curve. Data presented later show that these data are from the low-temperature range of a different current carrier. Activation energies

TABLE IV. Activation energies for conductivity in the MgO-NiO system.

Composition	High-temperature value, (eV)	Low-temperature value, (eV)
MgO	3.50	0.92
1.1% NiO-MgO	3.28	0.77
2.9% NiO-MgO	2.94	0.54
5.7% NiO-MgO	...	2.30
22.9% NiO-MgO	...	2.32

³ A. B. Lidiard, in *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246.

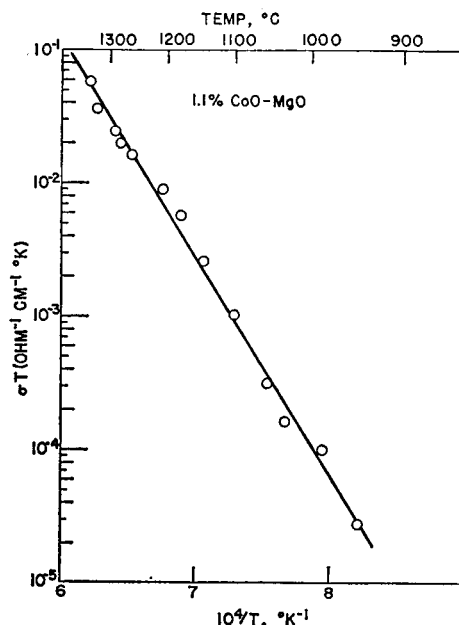


FIG. 5. Electrical conductivity data in CoO-MgO.

for conductivity obtained from both the high- and low-temperature slopes are presented in Table IV.

Similar data for 1.1% CoO in MgO are shown in Fig. 5 for the high-temperature portion. The activation energy for conductivity is 3.24 eV, a value close to that obtained with the 1.1% NiO specimens.

Possible changes from ionic conductivity to electronic conductivity might be expected to occur near the melting point with ionic oxides. Since the experimental

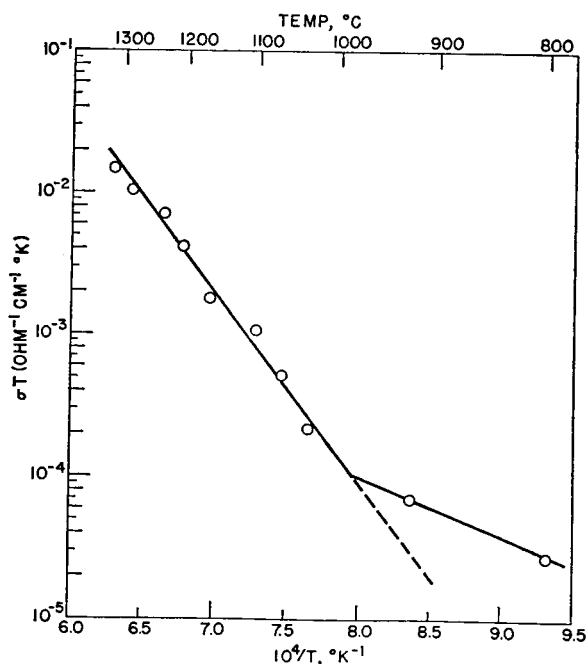


FIG. 6. Conductivity in aluminum oxide.

temperatures obtainable were far below the melting point of MgO, it was of importance to determine the conductivity of aluminum oxide, which has a considerably lower melting point. In many of its other properties, aluminum oxide is similar to magnesium oxide. It is another example of an ionic oxide. Disks of Triangle RR alumina were used as specimens. The results are presented in Fig. 6 to temperatures corresponding to 68% of the absolute melting point. The high- and low-temperature activation energies from these data are 2.66 and 0.68 eV, respectively. The curve otherwise was similar in appearance to that of MgO. As with the MgO, there was no indication of any further changes in slope at the highest experimental temperatures. The value 2.66 eV is small in comparison with the band gap for aluminum oxide. Since there is no change from ionic conductivity to electronic conductivity with Al_2O_3 , we would not expect such a change with MgO at temperatures corresponding to 51% of the absolute melting point.

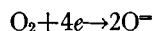
Our conductivity data presented above were obtained in argon containing oxygen as an impurity to the extent of approximately 0.001%. Quite different results are obtained in an atmosphere of argon containing 1.0% oxygen. These data for MgO are shown in Fig. 7. The high- and low-temperature activation energies are 5.22 and 2.67 eV, respectively.

DISCUSSION

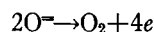
Nature of Conductivity in MgO

Several previous determinations of the electrical conductivity of magnesium oxide have been published.⁴⁻⁸ The mechanisms suggested by the authors have been radically different. The most nearly direct approach used to determine the nature of the conductivity is that of potential measurements. Other evidences as to the nature of the conductivity will also be discussed. They are especially useful at present in light of the contradictory results obtained from the potential measurements.

Measurements have been made of the potentials of oxygen concentration cells obtained by exposing opposite faces of MgO specimens to different oxygen partial pressures. If the mechanism of conductivity in the oxide is ionic and if the electrode reactions are limited to



at one electrode and



at the other electrode, then the potential obtained

⁴ R. Mansfield, Proc. Phys. Soc. (London) **B66**, 612 (1953).

⁵ A. Lempicki, Proc. Phys. Soc. (London) **B66**, 281 (1953).

⁶ E. Yamaka and K. Sawamoto, J. Phys. Soc. Japan **10**, 176 (1955).

⁷ W. Weigelt and G. Haase, Ber. Deut. Keram. Ges. **31**, 45 (1954).

⁸ S. P. Mitoff, J. Chem. Phys. **31**, 1261 (1959).

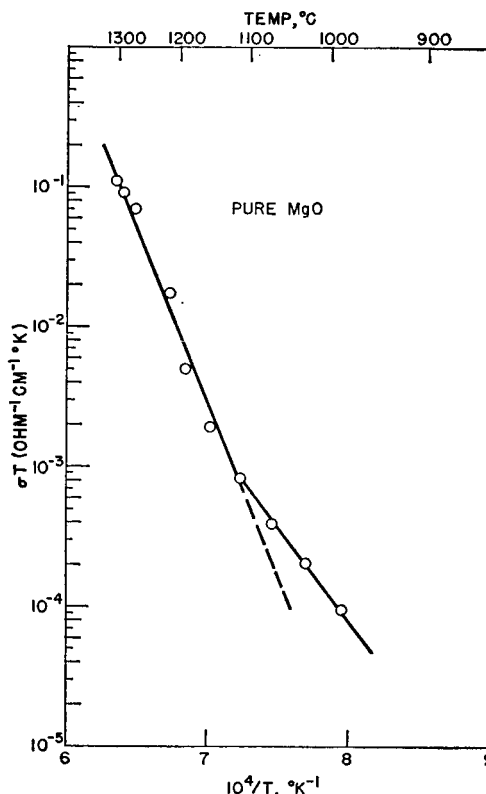


FIG. 7. Conductivity in argon containing 1.0% oxygen.

should be that calculated from the Nernst equation

$$E = (RT/4F) \ln(P_2/P_1),$$

where P_2 and P_1 are the two oxygen pressures.

Schmalzried found that at 1100°C the conductivity in MgO was predominantly ionic⁹ and quoted references that seemed to indicate that MgO also possessed predominantly ionic conduction at temperatures above 1100°C. He obtained the two differing oxygen partial pressures from Fe, FeO and Ni, NiO pellets. His experiment involved measuring the open circuit voltage of a cell consisting of a single crystal of magnesium oxide placed in contact with the Fe, FeO and Ni, NiO pellets. The voltage obtained was close to the value obtained in a similar cell in which the known ionic conductor ZrO_2 (stabilized in the cubic phase with CaO) was used instead of MgO.

Experimental potential measurements have also been reported by Mitoff.^{10,11} In his last paper,¹¹ Mitoff has used various gas mixtures to obtain the differing oxygen partial pressures on the two sides of the MgO single crystal. His results seemed to indicate that the percentage of ionic conduction decreased rapidly as the temperature of measurement increased from 1000° to 1500°C.

⁹ H. Schmalzried, J. Chem. Phys. **33**, 940 (1960).

¹⁰ S. P. Mitoff, J. Chem. Phys. **33**, 941 (1960).

¹¹ S. P. Mitoff, J. Chem. Phys. **36**, 1383 (1962).

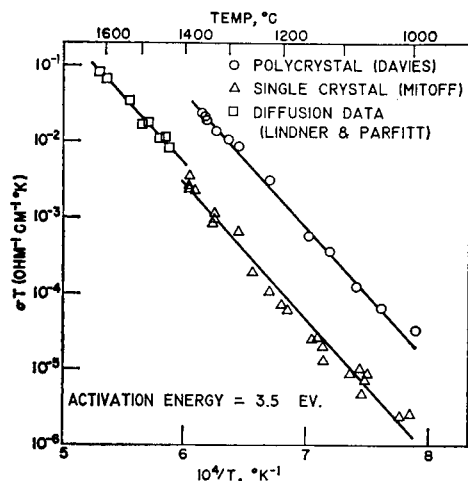


FIG. 8. Conductivity of MgO; cases representing magnesium ion motion.

On the other hand, Pal'guez and Neuimin,¹² using polycrystalline specimens of MgO, found that the percentage of ionic conduction changed little with temperature in the temperature range 1050° to 1300°C, and that its value was close to 100% (92.8% to 95.7%) when oxygen and a mixture of 66 vol. % CO + 34 vol. % CO₂ were used to fix the partial pressures of oxygen on the two sides of the specimen. When oxygen and air were used as the two gases, somewhat smaller values of percentage of ionic conductivity were found in the temperature range 1100° to 1300°C, but the values increased with increases of temperature, reaching 87.2% at 1300°C.

The exact reason for the differing results between investigators cannot be definitely stated at present, but a possible explanation for lower experimental potentials could be that they are mixed potentials because of chemical reactions of the other gaseous components with the MgO (or with an impurity in the MgO). With the smaller surface areas exposed to the gas streams by single crystals in comparison to polycrystals, even greater care must be exercised in the potential measurements on single crystals in order to prevent possibly even unsuspected impurities (in gas, electrode, or electrolyte) from completely changing the nature of the process being studied. If more than one potential determining reaction is occurring, it is not possible to ascribe the differences between theory and experiment solely to electronic conductivity. Further studies using carefully purified argon-oxygen mixtures and the best MgO crystals available would seem to be most helpful in resolving the conflict in the potential measurements. Such experiments, however, even when completed, will not permit one to determine which ion is the primary current carrier.

Comparison of electrical conductivity data with self-diffusion data can be used to answer this question. We

will assume that the same mechanism is operative if the activation energies are the same. Fortunately, self-diffusion data are available both for magnesium ion¹³ and for oxide ion.¹⁴ The Mg⁺⁺ data are from the intrinsic region; the O⁼ data are in the impurity controlled or extrinsic region. By the use of the activation energy criterion, one can separate the published conductivity data for MgO into two groups. (It is important to use the original data.) The group having the same activation energy as that obtained for Mg⁺⁺ diffusion is plotted in Fig. 8. The second group, agreeing with that for oxide ion diffusion, is shown in Fig. 9. Thus, the predominant current carriers may be either cations or anions. The Nernst-Einstein equation, with an assumed value for the transference number of 1, has been used to convert diffusion data to conductivity data so that the diffusion data could be plotted in these same figures. The conductivity data from Fig. 9 were all obtained *in vacuo* or under an extremely small oxygen pressure (10⁻⁸ atm).

When one compares the single crystal conductivity data of Fig. 8 with conductivity data calculated from the Mg⁺⁺ self-diffusion data, one notes that the two agree not only in activation energy, but agree closely in magnitude as well. This is one of the strongest indications that the electrical conductivity of MgO is ionic.

It is also of importance to note that the activation energy from the Weigelt and Haase conductivity data not only agrees satisfactorily with the activation energy for oxygen ion self-diffusion but the data are linear over the temperature range from 700° to 1800°C (cf. Fig. 9). This would seem to imply that an ionic conductivity

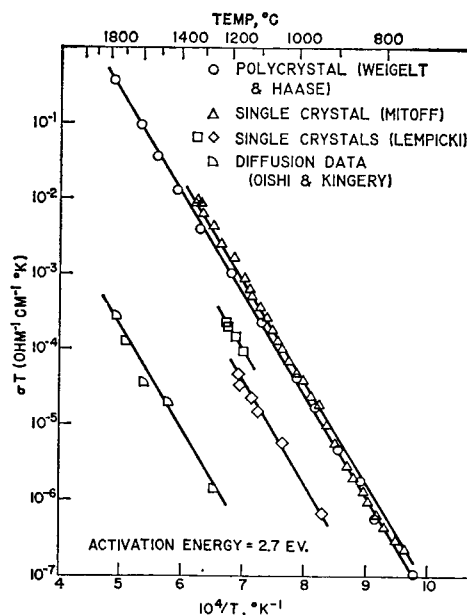


FIG. 9. Conductivity of MgO; cases representing oxygen ion motion.

¹² S. F. Pal'guez and A. D. Neuimin, *Fiz. Tverd. Tela*, **4**, 855 (1962).

¹³ R. Lindner and G. D. Parfitt, *J. Chem. Phys.* **26**, 182 (1957).

¹⁴ Y. Oishi and W. D. Kingery, *J. Chem. Phys.* **33**, 905 (1960).

mechanism based on oxygen ion motion predominated over that complete temperature range. Weigelt and Haase prepared their best MgO by carefully oxidizing 99.99% Mg metal in carefully purified oxygen gas. Since their conductivity measurements were made *in vacuo*, extrinsic oxygen ion conductivity resulted.

Our data for conductivity of MgO in argon with 1.0% O₂ possess an activation energy for the low-temperature portion, which also agrees with the activation energy for oxygen ion self-diffusion. The high-temperature activation energy, 5.22 eV, is believed to be the intrinsic activation energy for oxygen ion conductivity. Such an activation energy has not been previously reported.

At this point, it is worthwhile to summarize the activation energies which have been obtained for the electrical conductivity of MgO. The four activation energies obtained from the present investigation are 5.2, 2.7, 3.5, and 0.92 eV. These seem to be the activation energies, respectively, for intrinsic oxygen ion conductivity, extrinsic oxygen ion conductivity, intrinsic magnesium ion conductivity, and extrinsic magnesium ion conductivity. The energy of formation of Schottky pairs has been calculated from the high- and low-temperature activation energies for various compositions and is presented in Table V. The agreement between the two sets of values for MgO lends support to the identification presented above. Further support comes from a comparison of the values to those of NaCl. The ratio of intrinsic activation energies for conductivity in MgO is $Q(\text{O}^-)/Q(\text{Mg}^{++}) = 5.22/3.50 = 1.49$. In the intrinsic range for self-diffusion in NaCl, the ratio for activation energies is $Q(\text{Cl}^-)/Q(\text{Na}^+) = 2.23/1.60 = 1.39$. The ratio for MgO would be expected to be larger than 1.39 since the ionic radius ratio of anion to cation is larger for MgO than for NaCl.

Transference number determinations are in general not useful in determining the nature of the conductivity in pure compounds such as MgO. There are great difficulties in even defining what is meant by the term. One cannot neglect the nature of the electrode reaction when making dc measurements, whether conductivity measurements or transference number determinations. In the ideal case, if one uses electrodes that are reversible solely to the cation, one will obtain a transference number for the cation of 1; if one uses electrodes that are reversible solely to the anion, one will obtain a transference number for the anion of 1; if, on the other hand, one uses electrodes which are reversible to neither cation nor anion, both electrodes will polarize and electronic conductivity can result. Actually, in practice, it would seem to be possible to get any combination of the three. But, even of more importance, how one sets up the experiment and how one performs the measurements will unambiguously determine what result will be obtained. In short, one is biasing the result by how one makes the measurement! (Any result is possible from transference number measurements on pure compounds, even for the same or comparable specimens.)

TABLE V. Energy of formation of Schottky pairs.

	From +ion motion, (eV)	From -ion motion, (eV)
MgO	5.2	5.1
1.1% NiO-MgO	5.0	...
2.9% NiO-MgO	4.8	...
Al ₂ O ₃	5.0	...

Furthermore, if side reactions are occurring somewhere in the system, the experimental results may change as a function of time during any one determination.

Role of Grain Boundaries

When we compare our data for pure MgO with data from Mitoff's purest single crystal, we find that the activation energies from both regions (above and below the knee) are the same although the polycrystal conductivity is larger by approximately one order of magnitude. The agreement of activation energies in both regions between polycrystal and single crystal would certainly seem to indicate that the mechanism of conductivity was the same in polycrystal and single crystal. The problem is one of explaining this variation in the pre-exponential for constant activation energy. We should also note from Fig. 9 the variation of conductivity values among investigators without change of activation energy and the large difference between these conductivity data and values calculated from diffusion data.

Such an effect is not restricted to MgO. Barr *et al.*¹⁵ and Laurent and Bénard¹⁶ have observed similar phenomena in diffusion studies in the alkali halides. Both groups observed diffusion coefficients that appeared to be for simple volume diffusion but which at the same time depended upon, respectively, dislocation density or grain boundary density in the crystals. Laurent and Bénard state that the essential factor seemed to be the capability of the ion to be deformed by the field of asymmetric force which prevails in the boundary of the crystalline domains. The more the ion is polarized, the greater the influence of the intercrystalline surfaces and dislocations, irrespective of the polarity of the diffusing ion. When one compares diffusion data and conductivity data of MgO, the effect should be more prominent with oxygen ion conductivity than with magnesium ion conductivity, as is actually the case. However, even with Mg⁺⁺ conductivity, such an effect can explain the higher conductivity obtained with small grain polycrystals in comparison with the single crystal data.

Little is known of the nature of grain boundaries and dislocations in ionic crystals. Nevertheless, it is

¹⁵ L. W. Barr, I. M. Hoodless, J. A. Morrison, and R. Rudham, *Trans. Faraday Soc.* **56**, 697 (1960).

¹⁶ J. F. Laurent and J. Bénard, *J. Phys. Chem. Solids* **7**, 218 (1958).

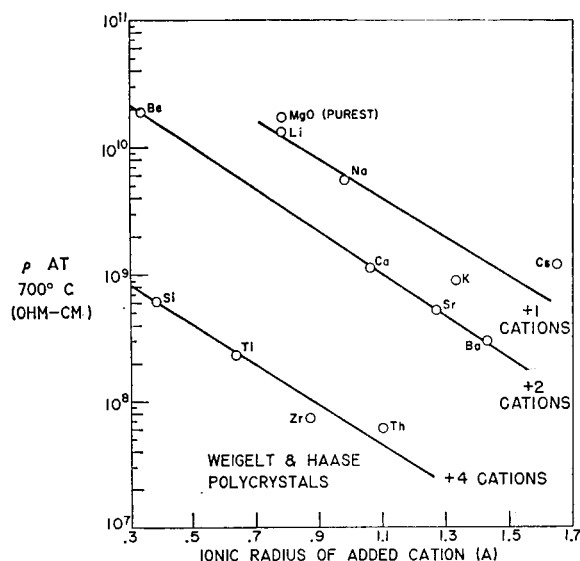


FIG. 10. Conductivity in MgO with 1% additions of various oxides.

quite likely that they are electrically charged.¹⁷ If this be the case, vacancies of the opposite charge should be present in higher numbers in the region close to the grain boundary or dislocation, and an increase in conductivity or diffusion coefficient would result. The region affected by each boundary could possibly be as large as a micron in size. For small grain polycrystals, such as used in this investigation, this would mean that an appreciable fraction of the volume of the specimen would be affected. It is of interest to note that Laurent and Bénard showed that diffusion of anions can occur preferentially in regions near intercrystalline boundaries. The conditions for uniform bulk diffusion (or conductivity) in ionic solids possibly may not yet have been obtained experimentally. The agreement of activation energies between single and polycrystalline samples indicates that the same mechanism is operative in both. It does not prove that the conductivity takes place uniformly throughout the bulk with either polycrystal or single crystal. Yet this mechanism of conduction is not what is normally referred to as grain boundary conductivity.

Possible Mechanisms for Oxygen-Ion Conductivity

Although one would expect cation conductivity to predominate in MgO on the basis of ion size, far fewer cases of conductivity representing magnesium ion motion have been reported than cases representing oxygen ion motion. As has been shown above, how one makes the experimental measurements can have a profound

influence upon the results obtained. In particular, the atmosphere used seems to be of the utmost importance.

We find conductivity predominantly by oxygen ions in the presence of high concentrations (1%) of oxygen gas. This is exactly the opposite of what might be expected on the basis of current theories of electrical conductivity. However, such a result does not seem to be restricted solely to polycrystals. Mitoff¹¹ has obtained dc conductivity measurements in an oxygen atmosphere on two single crystals of MgO that were less pure than those used to obtain the data shown in Fig. 8. The data represented by the squares in Fig. 2 of his paper, when plotted on a $\log \sigma T$ -vs- $1/T$ plot, are reasonably linear. They possess an activation energy of 2.72 eV and seem to represent extrinsic oxygen ion conductivity.

Although the mechanism by which oxygen ion conductivity occurs in the presence of oxygen gas is not known, certain possibilities can be mentioned. It is possible that the presence of oxygen gas leads to the formation of a space charge at the surface of the grains and that the conductivity takes place preferentially in the space-charged region. Under these conditions we would expect the surfaces to be negatively charged and to attract oxygen vacancies (with net positive charge) to the vicinity. Alternatively, the conduction might result from the motion of a triple vacancy composed of two single magnesium and one oxygen vacancy. This latter possibility would alleviate the problem of how oxygen ions could find room to move in a lattice in which the lattice spacing results from anion-anion repulsion.

The conductivity data of Weigelt and Haase⁷ seem to provide a clue as to the direction that theory may need to take in order to explain the experimental conductivity data. In addition to conductivity data for pure MgO, Weigelt and Haase also obtained conductivity data for a number of specimens of MgO to which 1 mole % of various impurity oxides was added. The additive oxides included ones with various +1, +2, and +4 cations. An example of the data obtained (at 700°C) is shown in Fig. 10. From the activation energies for conductivity, it is evident that Weigelt and Haase were getting extrinsic oxygen ion conductivity in almost every case through a very wide temperature range. The dependence of conductivity upon ionic radius of the added cation, as shown in Fig. 10, is most intriguing. Furthermore, we note that the larger the valence of the added cation, the larger is the increase in conductivity. Such a dependence on valence is strongly reminiscent of the effects noted in aqueous solutions approximately described by equations derived from Poisson's law such as the Debye-Hückel-Onsager equation. There seems to be nothing inherent in Poisson's law to prevent its application to solid electrolytes such as MgO, even though certain assumptions involved in the derivation of the Debye-Hückel-

¹⁷ P. L. Pratt, in *Symposium in Vacancies and Other Point Defects in Metals and Alloys* (The Institute of Metals, London, 1958), p. 99.

Onsager equation itself are not valid for solid electrolytes.

Comparisons of Other Oxides with MgO

Activation energies for conductivity near the 2.7-eV activation energy observed with MgO have also been observed for other oxides. All such cases should be closely investigated since the possibility of oxygen ion conductivity should not be restricted solely to MgO. Three such cases are described below.

Lindner has determined the electrical conductivity of CaO compacts using an air atmosphere.¹⁸ His data yield an activation energy of 2.76 eV. This does not agree with the activation energy for Ca^{++} self-diffusion of 3.5 eV, which he also determined.¹⁸ His transference numbers for Ca^{++} in CaO under the same conditions (of an air atmosphere) varied from 10^{-3} to 10^{-2} . We would expect such low values for Ca^{++} transference numbers since the magnitude of the activation energy seems to indicate oxygen ion conductivity rather than calcium ion conductivity. This is apparently another case of oxygen ion conductivity in an atmosphere containing large amounts of oxygen gas.

The activation energies for the 5.7% and 22.9% NiO specimens, 2.3 eV, are in satisfactory agreement with the oxygen self-diffusion data of O'Keefe and Moore for pure NiO.¹⁹ This would seem to indicate that both the conductivity and diffusion must proceed by an oxygen ion mechanism of some type. Apparently the presence of Mg^{++} prevents the formation of an electronic conduction band such as is found with pure NiO since the introduction of even this much NiO into MgO does not seem to lead to electronic conduction.

Pappis and Kingery have recently determined the electrical conductivity of single crystals of aluminum oxide in atmospheres with different oxygen partial pressures.²⁰ With 10^{-5} atm of oxygen present, they observed low- and high-temperature activation energies of 2.6 and 5.5 eV; with 10^{-10} atm, 2.8 and 5.8 eV. The 5.8-eV activation energy is in excellent agreement with the 5.85-eV activation energy obtained from the sintering studies of Kuczynski *et al.* on aluminum oxide

spheres.²¹ If the activation energies are identified as extrinsic and intrinsic oxygen conductivity activation energies, one obtains 4.8 and 4.9 eV for the energy of formation of Schottky pairs. These values are in satisfactory agreement with the 5.0-eV value obtained from our conductivity data presented above. Oishi and Kingery²² have presented some data for oxygen ion self-diffusion in Al_2O_3 . The value of the activation energy from these data is, however, very uncertain because of the extremely large scatter in the data. Further oxygen ion diffusion experiments on both single crystals and polycrystals of Al_2O_3 would be most useful.

CONCLUSIONS

Although the use of activation energies is not a completely satisfactory criterion for determining the mechanism of transport phenomena, it seems to be the best one available at present. In light of this criterion, MgO conductivity data possess features which can be satisfactorily explained by ionic mechanisms of conductivity. The available conductivity data all seem to lead to a consistent picture. With polycrystalline specimens, the type of current carrier is dependent upon the partial pressure of oxygen. There is an intermediate partial pressure region in which magnesium ions seem to be predominant current carriers. At higher and lower oxygen partial pressures, oxide ions seem to be the predominant current carriers. The mechanism of conductivity is the same with single crystal MgO and polycrystal MgO. The presence of grain boundaries increases the magnitude of the conductivity but does not seem to change the mechanism of conductivity from that observed with single crystals. Conductivity data for aluminum oxide, calcium oxide, and certain mixed oxides of MgO and NiO and of MgO and CoO can also be interpreted in terms of ionic mechanisms of conductivity.

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¹⁸ R. Lindner, *Acta Chem. Scand.* **6**, 468 (1952).

¹⁹ M. O'Keefe and W. J. Moore, *J. Phys. Chem.* **65**, 1438 (1961).

²⁰ J. Pappis and W. D. Kingery, *J. Am. Ceram. Soc.* **44**, 459 (1961).

²¹ G. C. Kuczynski, L. Abernethy, and J. Allan, *Kinetics of High-Temperature Processes* (Technology Press, Cambridge, Massachusetts, and John Wiley & Sons, Inc., New York, 1959), Chap. 21, p. 163.

²² Y. Oishi and W. D. Kingery, *J. Chem. Phys.* **33**, 480 (1960).