

Ionic Conductivity of Tantalum Oxide at Very High Fields

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The abnormally long jump distance λ which characterizes the ionic conduction of glasses as a function of electric field, $\sigma = \sigma_0 \exp(-q\lambda E/kT)$, and the fact that for tantalum oxide this distance changes by a factor of two at a critical field are explained in terms of a model in which ionic conduction is a two-stage process involving the creation and motion of interstitial metallic ions. Below a critical field both the number of interstitial ions and their mobility are rapidly varying functions of the field and the jump distance decreases discontinuously as the field increases. Above the critical field the number of interstitials depends much less strongly or not at all on the field, the field acts only to increase the ionic mobility, and the jump distance is of the order of the interatomic spacing. It is suggested that in tantalum oxide electrostatic repulsion between tantalum ions may provide the principle barrier to ionic motion.

WHEN subjected to very high electric fields during anodic oxidation, tantalum oxide exhibits ionic conduction that depends upon field through a relationship of the form

$$j = j_0 \exp[-(Q - q\lambda E)/kT], \quad (1)$$

where j is the current, j_0 and Q are constants, q is the charge on the moving ion, E is the electric field, λ is a distance of the order of a few angstrom units, k is Boltzmann's constant, and T is the absolute temperature.¹ Verwey² has related this expression for ionic conductivity to a diagram of the type sketched in Fig. 1 which shows the potential energy of an ion as it moves

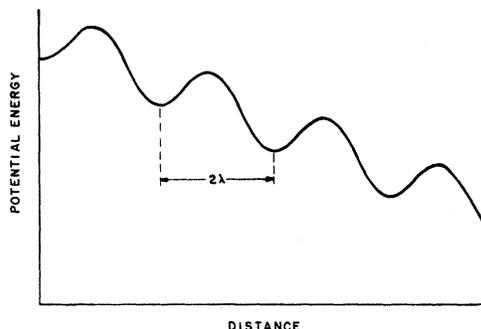


FIG. 1. Potential energy of an ion moving through an ionic solid under the influence of a strong electric field.

through an ionic solid under the influence of an applied electric field. The idea is that an ion at a potential energy minimum has negligible chance of jumping to the left in opposition to the applied field, and that it jumps to the right with frequency

$$\nu \exp[-(Q - q\lambda E)/kT],$$

where the zero-field activation energy Q has been reduced by the amount $q\lambda E$, which is the work done on the ion as it moves to the top of a potential-energy peak. Assuming the number of ions capable of carrying current to be independent of field, the ionic current in the

solid is proportional to this frequency, leading to Eq. (1).

For tantalum oxide¹ and for glass^{3,4} it is observed that the value of λ required to fit experimental observations of ionic conductivity often is at least double the value that would be expected from atomic dimensions. For tantalum oxide, the required value of λ changes by a factor of two at a field of about 6×10^6 volts/cm, as shown in Fig. 2.

It is evident that the simple theory based on the potential energy picture of Fig. 1 needs extension. We propose to alter it by showing that the number of charge carriers changes rapidly with field at large fields. Our

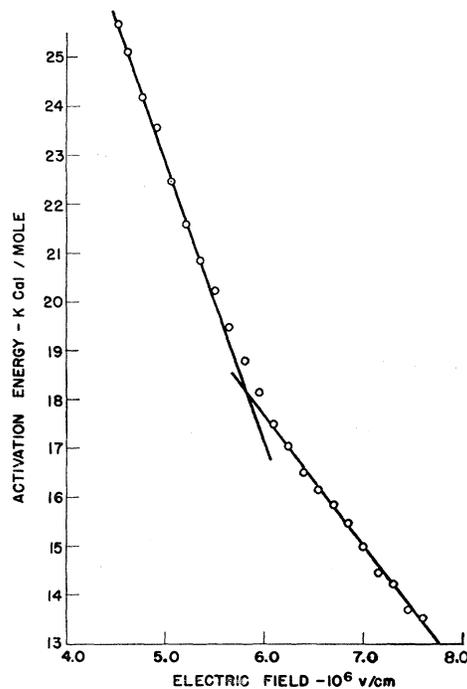


FIG. 2. Activation energy versus electric field for ionic conduction in anodic Ta_2O_5 films.

¹ D. A. Vermilyea, *J. Electrochem. Soc.* **102**, 655 (1955).

² E. J. W. Verwey, *Physica* **2**, 1059 (1935).

³ H. H. Poole, *Phil. Mag.* **42**, 488 (1921).

⁴ R. J. Maurer, *J. Chem. Phys.* **9**, 579 (1941).

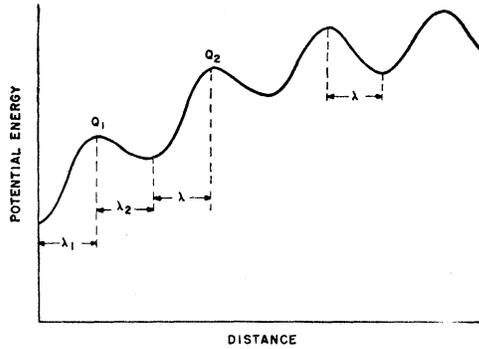


FIG. 3. Potential energy of an ion as it moves away from its equilibrium position into successive interstitial positions.

treatment is similar to that of Onsager,⁵ who discussed the field-enhanced dissociation of weak electrolytes, but is simpler because of the relatively small number of potential energy minima available to ions in a solid.

For concreteness, we consider an ionic crystal or glass in which the current is carried by interstitial metal ions. The potential energy plot for separating such an ion from its equilibrium position in the crystal or glass is sketched in Fig. 3 for zero field.

Because of the electrostatic interaction of the ion and the ion vacancy it leaves behind, the potential energy of an ion in the lattice is modified from that sketched in Fig. 1. At and beyond a distance $\lambda_1 + \lambda_2$ from the equilibrium position, the potential energy sketched in Fig. 1 is everywhere reduced by about q^2/kr , where r is the separation of the ion and vacancy and k is the dielectric constant. Closer than a distance $\lambda_1 + \lambda_2$ to the equilibrium position the ion and vacancy overlap, the macroscopic dielectric constant has less validity, and the q^2/kr energy reduction does not hold even approximately.

Application of a large field shifts the configuration sketched in Fig. 3 to that shown in Fig. 4, and a still higher field shifts it to that sketched in Fig. 5. The activation energy for the production of interstitial ions in Fig. 4 is $Q_2 - (\lambda_1 + \lambda_2 + \lambda)E$, corresponding to the height of the second potential barrier. At higher fields it shifts to $Q_1 - q\lambda_1 E$, corresponding to the height of the first potential barrier. It is this discontinuous shift of activation barrier with field that leads to the effects under discussion.

The number of free ions can be calculated by equating their rates of formation and annihilation. Because the fields are so high, two simplifying approximations can be made:

1. No ions jump against the field, except perhaps back over the first potential barrier in Fig. 4. It can be shown that negligible error is introduced by neglecting these jumps against the field.

2. The capture cross section of an ion vacancy for interstitial ions is independent of field at high fields, and is of atomic size.

⁵ L. Onsager, J. Chem. Phys. 2, 599 (1934).

With these simplifications, the rate at which interstitial ions are generated is

$$dn_+/dt = (N-n)\nu \exp[-(Q_i - q\lambda_i E)/kT], \quad (2)$$

where N is the equilibrium number of ion positions, n is the number of interstitial ions, ν is a frequency, Q_i is Q_1 or Q_2 , and λ_i is λ_1 when Q_i is Q_1 , $\lambda_1 + \lambda_2 + \lambda$ when Q_i is Q_2 . The rate at which they are annihilated is

$$dn_-/dt = (n^2/N)\nu \exp[-(Q - q\lambda E)/kT]. \quad (3)$$

Equating these values

$$n/N = (1 - n/N)^{\frac{1}{2}} \times \exp[-(Q_i - Q - q\lambda_i E + q\lambda E)/2kT]. \quad (4)$$

Because, in general, $\lambda_i \neq \lambda$ it follows that n is a function of the field E .

Setting $(1 - n/N)^{\frac{1}{2}} \approx 1$, the ratio n/N becomes

$$n/N \approx \exp\{-[Q_2 - Q - q(\lambda_1 + \lambda_2)E]/2kT\} \quad (5a)$$

for fields smaller than $(Q_2 - Q_1)/q(\lambda_2 + \lambda)$, and

$$n/N \approx \exp\{-[Q_1 - Q - q(\lambda_1 - \lambda)E]/2kT\} \quad (5b)$$

for fields larger than $(Q_2 - Q_1)/q(\lambda_2 + \lambda)$.

The ion flux per unit area is

$$j = 2\lambda\nu n \exp[-(Q - q\lambda E)/kT].$$

At (high) fields less than $E = (Q_2 - Q_1)/q(\lambda_2 + \lambda)$, this expression becomes

$$j = 2\lambda\nu N \times \exp\{-[Q + Q_2 - q(\lambda_1 + \lambda_2 + 2\lambda)E]/2kT\}, \quad (6a)$$

and at fields greater than $E = (Q_2 - Q_1)/q(\lambda_2 + \lambda)$ it becomes

$$j = 2\lambda\nu N \exp\{-[Q + Q_1 - q(\lambda_1 + \lambda)E]/2kT\}. \quad (6b)$$

These two expressions for j show that if $\lambda_1 = \lambda_2$, the rate of change of activation energy with field is halved at the field $E = (Q_2 - Q_1)/q(\lambda_2 + \lambda)$.

COMPARISON WITH EXPERIMENT

The value of $q(\lambda_1 + \lambda)/2$ taken from the high-field slope of the experimental curve of activation energy

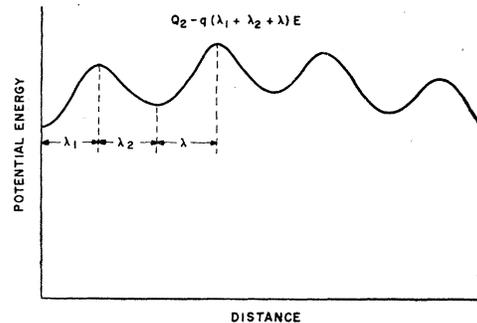


FIG. 4. The effect of a moderately strong electric field on the potential energy shown in Fig. 3.

versus field in Fig. 2 is $q(\lambda_1+\lambda)/2=11.8$ in units of $e \cdot \text{A}$, which, for a charge of $5e$, gives

$$\lambda_1+\lambda=4.72 \text{ A.} \quad (7a)$$

The low-field slope is double the high-field slope, giving $q(\lambda_1+\lambda_2+2\lambda)=23.4eA$, so that

$$\frac{1}{2}(\lambda_1+\lambda_2)+\lambda=4.68 \text{ A.} \quad (7b)$$

Equations (7a) and (7b) show that $\lambda_1=\lambda_2$. The zero-field intercepts of the two straight line portions of Fig. 2 give

$$\begin{aligned} Q+Q_1 &= 2.94 \text{ ev,} \\ Q+Q_2 &= 4.34 \text{ ev.} \end{aligned} \quad (8)$$

The calculated value of the pre-exponential factor $2\lambda\nu N$ is 5.6×10^{27} , assuming $\nu=5 \times 10^{12} \text{ sec}^{-1}$, whereas the experimental value drops from about 1.7×10^{27} at a field of 4×10^6 volts/cm to about 0.17×10^{27} at fields of 6×10^6 volts/cm and above. Although variation of the pre-exponential factor with field is not explained by our treatment, the degree of agreement between experiment and theory is satisfactory in view of the uncertainty in ν and in the interstitial-vacancy capture cross section, which was assumed constant and of single atomic size in deriving Eq. (4).

Two possible activation barriers to the motion of a tantalum ion will be discussed. First, oxygen ions may provide the activation barrier, tantalum ions squeezing between them from one octahedral position to another. In this event the values of λ_1 , λ_2 , and λ all are $a/2$, where a is the diameter of an oxygen ion. With $a \approx 2.9 \text{ A}$, the oxygen ion barrier gives $\lambda_1+\lambda \approx 2.9 \text{ A}$ and $\frac{1}{2}(\lambda_1+\lambda_2)+\lambda \approx 2.9 \text{ A}$, both of which are much smaller than the experimental value of 4.7 A .

Another possibility is that the activation barrier is provided by the electrostatic repulsions of other tantalum ions. Considering tantalum ions to be situated on a hypothetical close-packed lattice in a tantalum oxide glass of composition Ta_2O_5 , the distance between neighboring tantalum ions will be $b=a(5/2)^{1/2} \approx 3.9 \text{ A}$. The activation distance for one of these ions to move to an interstitial position in the tantalum ion lattice is about $\lambda_1=(\frac{2}{3})^{1/2}b \approx 3.2 \text{ A}$. The corresponding value of λ_2 is $\lambda_2=\lambda_1/2 \approx 1.6 \text{ A}$, and the activation distance for subsequent interstitial diffusion is about $\lambda=b/2 \approx 1.9 \text{ A}$. These values give $\lambda_1+\lambda \approx 5.1 \text{ A}$ and $\frac{1}{2}(\lambda_1+\lambda_2)+\lambda=4.3 \text{ A}$ in better agreement with the experimental value of 4.7 A . The calculated ratio of low-field slope to high-field slope of the activation energy with field is only $2(4.3)/5.1=1.7$, instead of 2.0 as observed, but in view of the degree of approximation in estimating λ_1 , λ_2 , and λ , discrepancies of this magnitude are not out of line.

The order of magnitude of the activation energy Q for the motion of an interstitial ion far from its origin was estimated very approximately as follows. It was assumed that the tantalum ions were arranged on a simple cubic array in a uniform sea of negative elec-

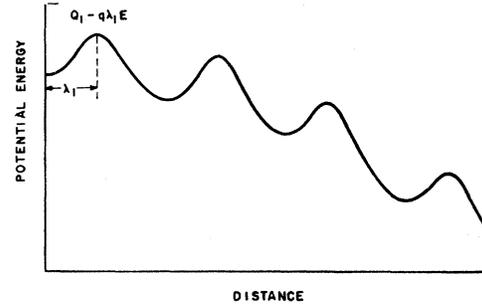


Fig. 5. The effect of a very strong electric field on the potential energy shown in Fig. 3.

tricity in a medium of the macroscopic dielectric constant. The electrostatic interaction energy between the interstitial tantalum ion and the lattice ions was calculated for an equilibrium position and at the saddle point between positions. The activation energy thus obtained was 1.0 ev . Estimates were also made of the activation energies Q_1 and Q_2 assuming that the tantalum ions were close packed and that each was surrounded by a spherically symmetric negative charge produced by 2.5 nearest-neighbor oxygen ions. This calculation gave 2.5 ev for Q_1 and 4.3 ev for Q_2 . While these values are to be regarded as very approximate, they do show that the assumption is reasonable that electrostatic interaction between tantalum ions provides the activation barrier.

For the conduction of sodium ions in glasses at temperatures in the vicinity of room temperature, experimental values for λ [Eq. (1)] range from about 15 to 60 A .^{3,4} The fields required to produce appreciable ionic motion were of the order of 10^6 volts/cm. Because of the smaller field and the smaller ionic charge the highest activation barrier for creation of a free sodium ion in a glass would be several atom distances from the ion, and hence a very large experimental value for λ is to be expected.

In view of the facts that Eqs. (6a) and (6b) for the current density fit the experimental observations in Fig. 2 when reasonable values of the parameters are employed, and that the correct absolute value of the current density also is obtained, we conclude that the conductivity mechanism we have proposed, with tantalum ions moving through the field of electrostatic repulsions provided by other tantalum ions, is reasonable.

To summarize this mechanism of conduction in tantalum oxide:

1. Current is carried by tantalum ions that form in the interior of the oxide, and that are "interstitial" with respect to a hypothetical tantalum ion lattice embedded in the tantalum oxide glass.

2. At fields below about 6×10^6 volts/cm, the activation energy for the formation of interstitial ions varies rapidly with field, because the activation barrier lies far from the origin of the ion. The field variation of the

recombination of interstitial ions and vacancies is less pronounced, leading to a concentration of interstitial ions that increases rapidly with field.

3. Above a field of about 6×10^6 volts/cm, the position of the activation barrier for interstitial ion formation moves discontinuously to a position near the origin of the ion, and the field dependencies of the activation energies for creation and recombination become more

nearly equal, so that the concentration of interstitial ions becomes less dependent upon field.

4. The influence of an electric field on the activation energy for ionic conductivity is twice as great at fields below 6×10^6 volts/cm as above, because at low fields both the number of charge carriers and their mobility is increasing with field, whereas above 6×10^6 volts/cm it is primarily their mobility that continues to increase.

Angular Dependence of the Characteristic Energy Loss of Electrons Passing Through Metal Foils*

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The Bohm-Pines electron plasma theory is employed to give a theoretical interpretation of some experimental results of Marton *et al.* on the scattering of 20-kev electrons by a thin gold foil. General criteria are presented which can in principle select in any given case between the alternative mechanisms of collective excitation or one-electron excitation. For the general case of collective excitation the scattering law is derived and used in a numerical analysis of the experimental data. Agreement with the Bohm-Pines theory is satisfactory.

I. INTRODUCTION

THE Franck-Hertz phenomenon in gases has long provided a tool, along with optical spectroscopy, for investigating the electronic energy level structure in gaseous atoms and molecules. The corresponding phenomenon in solids, because of technical difficulties, has been exploited more slowly. Rudberg¹ seems to be the first to have noticed that electrons of a few hundred volts, when reflected from solid samples of the noble metals, preferentially lose amounts of energy characteristic of the target metal. In each of these metals Rudberg found two characteristic energy losses, which we for short call "eigenlosses," all less than ten volts. Rudberg and Slater² interpreted these eigenlosses as one-electron interband transitions in which electrons occupying the filled *d*-band were excited to the top of the *s-p* band, thereby absorbing energy from and inelastically scattering the incident electrons. The discreteness of the loss spectrum arises from the "double-humped" character of the density of states curve for the filled *d*-band. There can be little doubt of the correctness of this interpretation, for it not only rests on some quite basic features of the band theory, but is also supported by the close correlation between the eigenlosses of Rudberg and the optical absorption peaks determined independently by Minor, and Meier.³ For example, the absorption of gold in the blue, which

causes its reddish color, has a maximum at 3700 Å, corresponding to a quantum energy of 3.36 eV. This agrees well with Rudberg's 3-volt eigenloss. Since the optical absorption is also due to the same mechanism of excitation of the *d*-band electrons, this agreement is necessary. In general, the hypothesis that a given eigenloss is a one-electron interband transition can be tested by examining the optical absorption data. If there is no absorption for light of quantum energy equal to the eigenloss, the interband hypothesis must be rejected in the specific case at hand.

Unfortunately, the optical absorption data are not very complete and it is not possible in practice to apply this test in very many cases. As already mentioned, Rudberg's low-energy eigenlosses for the noble metals pass the test. On the other hand, many eigenlosses discovered since Rudberg's early experiments do not satisfy this criterion. For example, there are no optical absorptions corresponding to the eigenlosses found by Marton and Leder⁴ for the alkali metals. In such cases the one-electron hypothesis must be abandoned in favor of a collective excitation involving the totality of the electrons in the metal. Collective phenomena lie outside the scope of the usual one-electron theory of metals, but are included from the start in the Bohm-Pines⁵ plasma theory of the free-electron gas. Modifications to take into account the interaction of the conduction electrons with the more tightly bound

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³ R. S. Minor, *Ann. Physik* **10**, 581 (1903), and W. Meier, *Ann. Physik* **31**, 1017 (1910).

⁴ L. Marton and Lewis B. Leder, *Phys. Rev.* **94**, 203 (1954).

⁵ D. Bohm and D. Pines, *Phys. Rev.* **92**, 609 (1953), and David Pines, *Phys. Rev.* **92**, 626 (1953).