

TABLE IV. Theoretical and experimental ionic mobilities.

Ion	Langevin mobility (hard sphere)	Experimental mobility (extrapolated)
Kr ⁺	1.01 cm ² /volt-sec	0.9-0.95 cm ² /volt-sec
Xe ⁺	0.77	0.6-0.65

atomic ions in agreement with the concept of weaker exchange forces. The cross sections for the atomic ion-atom collisions have been computed. They are some three times larger than the atom-atom cross sections. If the ion-atom collisions are largely charge exchange interactions, the large cross sections are in accordance with numerous direct measurements of this cross sec-

tion (at higher energies) which show increasing size with decreasing energy.⁶

The writer is most indebted to Dr. J. A. Hornbeck for placing at his disposal the equipment designed and constructed for the earlier work on helium, neon, and argon. He is also pleased to acknowledge the assistance and the helpful suggestions of Dr. David J. Rose. Mr. F. D. Dolezal also assisted materially in the work of assembly and of taking of data. Dr. Hornbeck and Dr. G. H. Wannier very kindly reviewed and helpfully criticized the analysis and the manuscript.

⁶ See, for example, Landolt-Bornstein, *Zahlenwerte und Funktionen* (Julius Springer, Berlin, 1950), Vol. 1, p. 358.

Conductivity of Oxide Emitters*

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Measurements of the conductivity of a BaSrCaO emitter over a range from room temperature to 1100°K indicate the existence, in well-activated cathodes, of a low temperature conduction mechanism having an activation energy of as little as 0.05 ev. Coincident with the temperature at which appreciable emission can be drawn, a high temperature conduction mechanism of 1 ev activation energy becomes evident. Application of a high pressure (25 atmospheres) of xenon to the cathode causes a marked decrease in conductivity in the high temperature range. These results are considered to confirm a hypothesis recently advanced by Loosjes and Vink that conduction in the high temperature region occurs predominantly through space currents in the pores of the oxide. The small activation energy of the low temperature conduction mechanism is considered to indicate the probability that this conduction occurs in a monolayer of barium on the surface of the oxide.

RECENT studies by Vink¹ and Loosjes and Vink² have led to the conclusion that the conduction through an oxide emitter, at operating temperature, occurs largely via space currents in an electron gas within the pore volume of the coating. In the present work, further evidence of conduction in this manner was sought.

The experimental approach has been to apply a relatively high pressure (25 atmospheres) of xenon gas to an activated emitter and to observe whether an apparent decrease in conductivity occurs. This method is based on the assumption that the electrons within the pores of the oxide will collide with the xenon molecules, and the average drift velocity under the influence of the applied field will be appreciably reduced.

The test cathode for measurement of resistance is of the design described by Loosjes and Vink, and is shown schematically in Fig. 1. A layer of oxide (BaSrCaO composition) of approximately 0.25-mm thickness is

held between the flat ends of two 3-mm diameter nickel cathode sleeves of "A" nickel, the sleeves being spring loaded to hold the assembly under slight compression. Oxide coating on the cylindrical surfaces of the sleeve and a closely spaced anode permit measurements of emission to be made. The porosity of oxide in a processed tube was determined to be 70 percent by volume. The temperature of the sleeves is measured by thermocouples. Connections to the sleeves permit measurement of the resistance of the oxide by means of a dc bridge. The test assembly is enclosed in a metal envelope of rugged construction and is connected to the vacuum system and a gas purifying train via glass to metal seals, as shown in Fig. 2. Manipulation of gas and vacuum is provided by glass tip-off constrictions and glass percussion valves.

The xenon is treated for removal of oxidizing impurities by prolonged exposure to glowing zirconium wire and a fluffy deposit of barium obtained by evaporation from "Batalum" getters in a low pressure of the xenon. The xenon can be transferred quantitatively to the envelope of the test cathode by freezing out in a side arm on the envelope. Tipping off from the gas train

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¹ H. S. Vink, thesis, Leiden (1948) (unpublished).

² R. Loosjes and H. J. Vink, Philips Research Reports 4, 449 (1949).

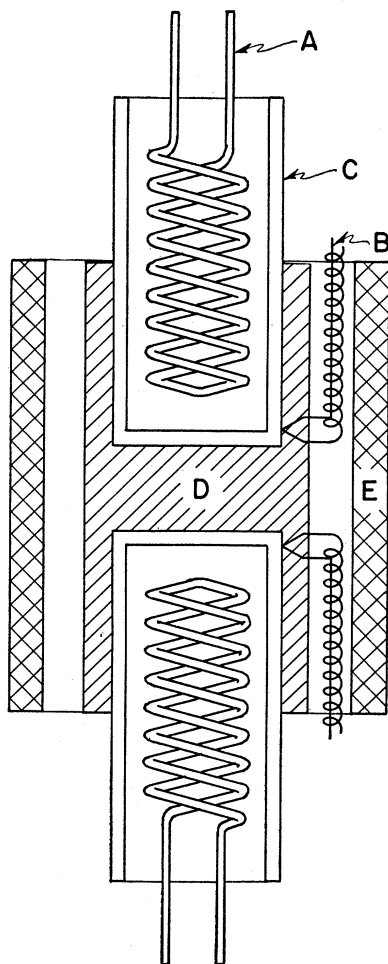


FIG. 1. Schematic representation of the experimental cathode. *A*—heater; *B*—thermocouple; *C*—nickel cathode sleeve; *D*—BaSrCaO; *E*—anode.

and expansion of the gas in the envelope volume then produces the desired pressure of 25 atmospheres. Subsequent measurements under vacuum conditions (pressure < 1 mm Hg) can be made by again freezing out the gas in the side arm by immersing in a liquid nitrogen bath.

Measurements of conductivity of the emitter as a function of temperature in the range from room to 800°C were made in the following sequence:

- (1) Tube on the pump and the oxide incompletely activated.
- (2) Tube "tipped off" and the oxide fully activated and stabilized.
- (3) Xenon admitted at $\frac{1}{2}$ atmosphere pressure.
- (4) Tube "tipped off" from the gas purifying train and xenon frozen out in the side arm.
- (5) Gas expanded in tube envelope to give 25 atmospheres pressure.
- (6) Gas alternately frozen out and expanded to check reproducibility of the observed pressure effects.

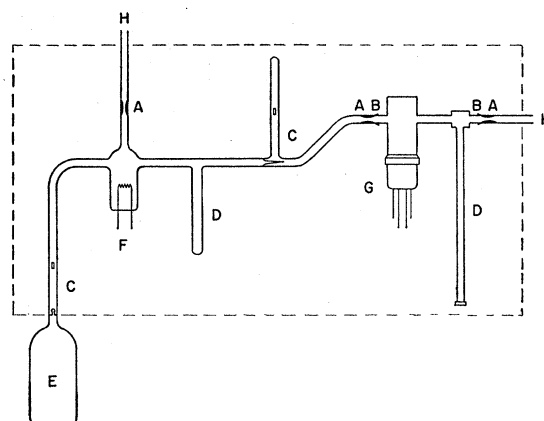


FIG. 2. The gas purifying train portion and experimental tube assembly. *A*—tip-off construction; *B*—Pyrex to Kovar seals; *C*—glass percussion valves; *D*—traps for freezing out xenon; *E*—flask of xenon; *F*—getters; *G*—experimental tube; *H*—leads to high vacuum system. The dotted lines indicate a bake-out oven.

Limited measurements of emission were made to determine the lowest temperatures at which significant emission (0.02 microampere or more) could be obtained.

EXPERIMENTAL RESULTS

Typical results of log conductivity *versus* reciprocal temperature (cathode in vacuum) are shown for three increasing degrees of activation in Fig. 3. Following activation of the cathode, and while the tube was still on the pump, plots *A* and *B* were obtained. These results, especially *A*, are very similar to those obtained

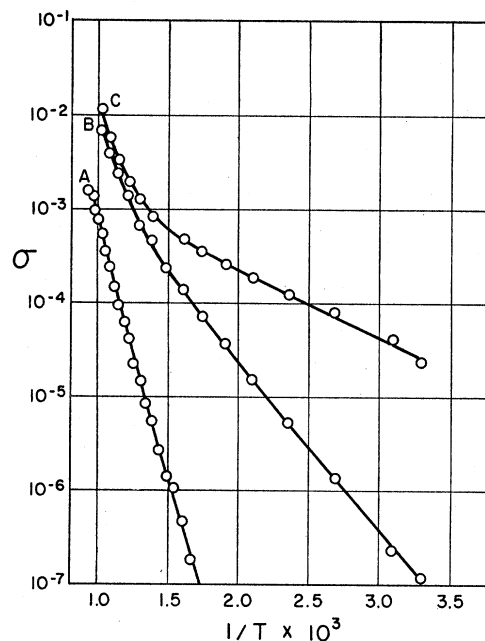


FIG. 3. Log conductivity *versus* reciprocal temperature relationships for an oxide emitter. *A*, *B*—tube on the pump, *B* more highly activated than *A*; *C*—tube tipped off.

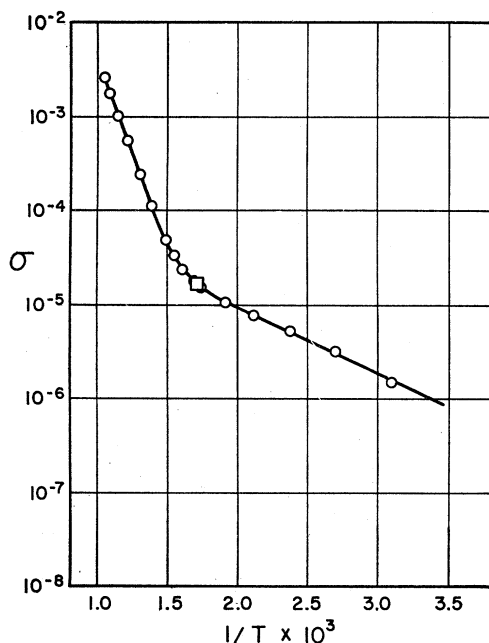


FIG. 4. Log conductivity *versus* reciprocal temperature relationships of oxide emitters. The tubes are tipped off and cathodes well activated. The point indicated by a square is the lowest temperature at which appreciable emission was obtained.

by Loosjes and Vink² on cathodes at the lowest state of activation. They are also similar to results presented by Hannay *et al.*³ and by Wright⁴ for measurements made with the tube on the pump. A comparison of activation energies and conductivities follows:

	Present work	Loosjes and Vink	Wright	Hannay <i>et al.</i>
Activation energy, ev	1.13	1.14	ca 1.1	1.1
Conductivity at 1000°K	10 ⁻³	6.3 × 10 ⁻³	3 × 10 ⁻⁴	4 × 10 ⁻⁴

A marked increase in conductivity, the appearance of a low temperature conduction mechanism of relatively low activation energy, and decrease in slope of the high temperature plot occur when the tube is tipped off, getters flashed, and the cathode held at 800°C until its resistance becomes stabilized. These effects are illustrated by curve C of Fig. 3.

Introduction of xenon at $\frac{1}{2}$ atmosphere pressure caused no significant change in the conductivity-characteristics of the cathode; likewise, results obtained when the gas pressure was reduced to a very low value by freezing the xenon out in the side arm were not significantly different. Therefore, the introduction of xenon and the tipping off to confine the gas within the cathode envelope has caused no significant change in state of activation of the cathode.

A typical plot representative of results obtained under vacuum, $\frac{1}{2}$ atmosphere, and low pressures conditions is presented in Fig. 4. The temperature at which appreciable emission (>0.02 microampere) could be

³ Hannay, MacNair, and White, *J. Appl. Phys.* **20**, 669 (1949).

⁴ D. A. Wright, *Brit. J. Appl. Phys.* **1**, 150 (1950).

drawn is indicated and is seen to coincide with the first detectable increase in conductivity above that of the low temperature plot. This is rather good evidence that the change in slope of the plot is associated with emission effects. Activation energies for representative measurements obtained on the pump and after tip off are given in Table I. These results are, in general, similar to those of Loosjes and Vink and confirm their conclusion that the high temperature conduction mechanism has an activation energy of approximately 1 electron volt.

Application of high xenon pressure produced a well-defined decrease in conductivity in the high temperature region. This is shown in Figs. 5 and 6. Subsequent removal of the xenon by freezing out restored the original vacuum and low pressure conductivity. Deviation between the vacuum and high pressure plots begins to occur at the temperature at which emission is detectable and becomes progressively greater as the temperature increases. The magnitude of change is by factors of 3 and 4 (approximately) for the two tubes at 700°C. Though the dependence of conductivity on xenon pressure at constant temperature could not be accurately examined, it was determined that the conductivity varied in a smooth manner as the gas pressure was changed. The changes produced in the low temperature range will be discussed subsequently.

On the logarithmic scale employed for presenting the data, it is not evident at first that the introduction of a high gas pressure has caused a large change in the conductivity of the coating. However, if we extrapolate the low temperature branch of the plot and calculate the proportion of current due to the low and high temperature mechanisms, we find at 700°C:

Tube No.	Tube No.	Description
673	524	2.8 1.6 percent of current carried by low temp. mechanism.
97.2	98.4	percent of current carried by high temp. mechanism, under vacuum conditions.
72	81	percent reduction in current carried by high temp. mechanism, due to high gas pressure.

TABLE I. Activation energies calculated from log conductivity *versus* reciprocal temperature.

Tube No.	Condition	Activation energy, electron volts		
		Low temperature mechanism	Uncorrected high temperature mechanism	High temperature mechanism, corrected for low temperature mechanism
524	on pump	...	1.13	...
	tipped off	0.13	0.68	0.94
	tipped off	0.13	0.76	0.99
	low pressure	0.13	0.76	0.99
	low pressure	0.14	0.71	0.94
673	on pump	0.31	0.86	1.24
	on pump	0.37	0.77	1.17
	tipped off	0.15	0.73	0.95
	tipped off	0.14	0.68	0.94
	tipped off	0.15	0.66	0.90
	tipped off	0.14	0.71	1.04

It is to be expected that, as the gas pressure is increased, emission currents in the large pores will at first be somewhat reduced and that, as the pressure is further increased, the effect will extend to successively smaller pores and that the degree of reduction in pores previously affected will become more marked. It is thus not to be expected that the space currents within the pores will be completely eliminated. The manner of deviation between the high and low pressure curves is therefore in qualitative agreement with what might be expected.

The emission which could be drawn to the plate was strongly decreased by the introduction of $\frac{1}{2}$ atmosphere of xenon. For example, at 450°C , in vacuum, 15 microamperes was obtainable; after introduction of $\frac{1}{2}$ atmosphere pressure, 0.02 microampere could be drawn at the same temperature and plate voltage. This is a change of nearly 3 orders of magnitude. No significant change occurred in the resistance. This furnishes strong evidence that the resistance measurements are free of any spurious space current effects external to the coating volume, for the distances which must be involved in such currents are comparable to the cathode to plate separation.

DISCUSSION

It remains to account for the discrepancy between the results obtained here and those of Hannay *et al.* Hannay's results were all obtained from tubes on the pumps, and without getters. Under these conditions we likewise obtain curves (see Fig. 3, curve A) in which the entire plot can be represented by an approximately straight line, and if two conduction mechanisms are present, these are not evident. This type of plot has

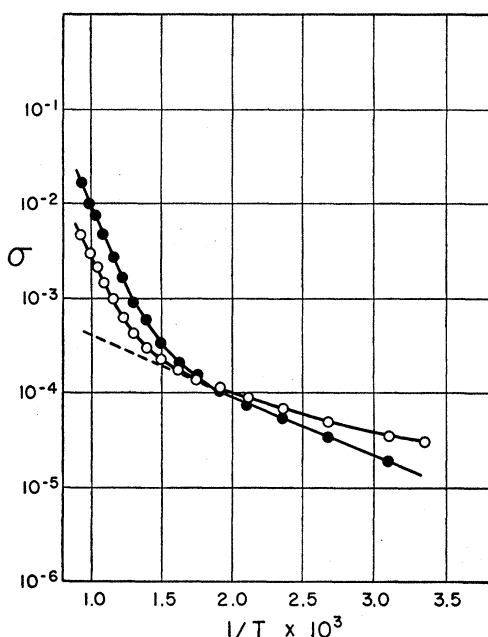


FIG. 5. Effect of high xenon pressure on conductivity of an oxide emitter. ●—vacuum and low pressure; ○—high pressure (25 atmospheres).

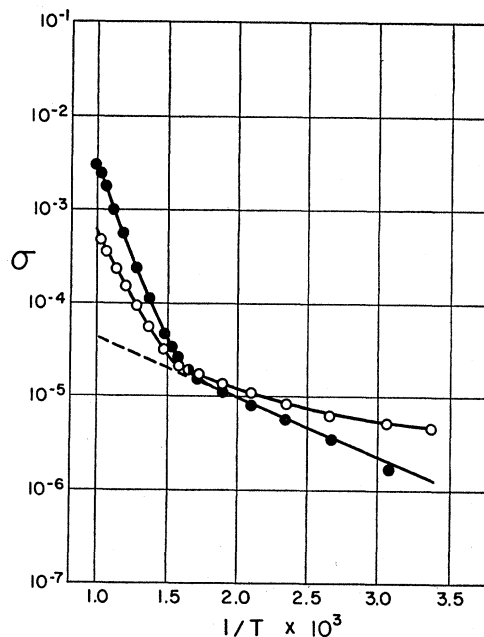


FIG. 6. Effect of high xenon pressure on conductivity of an oxide emitter. ●—vacuum and low pressure; ○—high pressure (25 atmospheres).

been discussed in detail by Wright⁴ who has observed that with any type of coating immediately after outgassing at 1300°K , a state is at once established, where σ is near $10^{-3}\Omega^{-1}\text{cm}^{-1}$ at 1100°K and where the slope of $\log\sigma$ versus $1/T$ is about 1.1 ev. Wright considers this an intermediate state, neither fully activated, nor poisoned. It is to this condition that a cathode tends to return after either poisoning in an oxidizing gas or activating in a reducing gas.

Comparing results obtained by different experimenters, we find that our results for the most inactive state on the pumps are closely similar to those described by Wright, an activation energy of 1.13 ev being obtained in our measurements. We concur with Wright in his belief that Hannay, McNair, and Wright have observed only this same state. We believe that Hannay *et al.* have obtained a low state of activation due to the fact that all measurements were made "on the pump," and because the activating agent employed, methane, is largely disassociated and consequently does not have the assumed effectiveness as a reducing agent. Further, operation at abnormally high temperature would have caused loss in activation both by barium evaporation and by sintering. As a result of these effects, the emission densities observed were less, by more than two orders of magnitude, than is normal for a "good" cathode. The present authors therefore conclude that the measurements of Hannay *et al.* do not represent the behavior of a well-activated cathode. The origin of the measured conductivity is not entirely evident but may well be almost entirely due to space currents in the pores of the coating.

A totally unexpected influence of the high gas pressure was noted in the low temperature branch of the conductivity plot. The conductivities are approximately equivalent for vacuum and high pressure conditions at the temperature at which emission is first detected but toward lower temperatures the vacuum and high temperature plots diverge significantly. Conductivity is increased in the low temperature region by the presence of the gas. In order to explain this fact satisfactorily it must be assumed that the low temperature conduction is determined by the surface properties of the oxide particles. It is most attractive to assume a monatomic layer of barium, as postulated by de Boer.⁵ At low temperatures this surface layer of barium might be oxidized by residual gases coming from various tube surfaces at a rate greater than arrival of fresh barium from the interior of the grains by diffusion. A layer of surface barium to account for the low temperature conduction has recently been suggested by Wright⁴ and by Friedenstein *et al.*⁶ This assumption would also explain the general failure of all observers to detect a low temperature conduction mechanism of low slope in all cases in which measurements are made on the pumps, for under these circumstances, a monatomic barium film would be most rapidly oxidized.

The effect of a high pressure of inert gas surrounding the cathode would be to greatly impede access of oxidizing gases coming from the tube walls. The gas pressure

⁵ J. H. de Boer, *Electron Emission and Absorption Phenomena* (Cambridge University Press, London, 1935).

⁶ Friedenstein, Martin, and Munday, Repts. Progr. Phys. **11**, 298 (1948).

should also reduce the rate of outgassing of the tube parts. If we assume further that protection of the surface film of barium from oxidation is never perfect, then the continuous curvature of the low temperature, high pressure plot and the rather slow increase in conductivity with increasing temperature is consistent with the view that the proportion of surface coverage is increased with increasing temperature as a consequence of the increased rate of barium diffusion. As an alternative to the assumption of an adsorbed monolayer of barium in the above speculations, one might attribute the low temperature conduction to semiconductor effects at points of contact between individual oxide crystals, the semiconductor being oxide activated by excess barium, and consider deactivation of the semiconductor by conversion of excess barium to oxide. However, the slope of the low temperature plot for the high pressure measurements decreases to 0.05 and 0.08 ev, respectively, for the two tubes. These low activation energies appear to be inconsistent with a semiconductor interpretation. In view of this low apparent slope, the supporting considerations by Wright and Friedenstein *et al.*, and the presumed efficacy of the gas in retarding the surface deactivation of the cathode, it appears most probable that the low temperature conduction is due to an adsorbed monolayer of barium.

This investigation was suggested by E. S. Rittner, to whom we are indebted for helpful discussions throughout the course of the work. Technical assistance by Richard Ahlert, George Beutel, and Martin Miller is also gratefully acknowledged.

The Close Pair Effect in Cosmic-Ray Stars*

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Evidence is presented to establish the existence of the close pair effect in cosmic-ray stars formed in nuclear emulsions exposed at 95,000 ft. A reasonable estimate of the magnitude of the effect may be derived from the data obtained, and this magnitude is compared with that obtained from similar studies at lower altitudes. It appears that a maximum for the excess of close pairs occurs for separations ≤ 1 mm in the emulsions exposed at balloon altitudes. It is extremely difficult to explain the effect on the basis of present knowledge.

INTRODUCTION

INDEPENDENTLY and almost simultaneously, Leprince-Ringuet and Heidmann¹ and Li and Perkins,² in 1948, discovered, in the analysis of a number of nuclear plates that had been exposed at about 12,000 ft in the Alps, that there were more pairs of stars with

small separations between their centers (on the order of hundreds of microns) than could be explained on the basis of a random distribution. Since the numbers involved in these studies were relatively small, it was felt that further studies were indicated both at comparable and other altitudes. The present study involves a balloon exposure of 8 hours at 95,000 ft and geomagnetic latitude 55°N.

In analyzing the 19 plates that were selected for this study, it was discovered that about 50 percent fewer stars fell in the border areas of the plates than were to

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¹ L. Leprince-Ringuet and J. Heidmann, *Nature* **161**, 844 (1948).

² T. T. Li and D. H. Perkins, *Nature* **161**, 844 (1948).