The Electrical Behavior of Thin Metallic Films Condensed at Low Temperatures

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The change of resistance of thin films of zinc and cadmium condensed at low temperature has been studied. The resistance of a zinc film decreases irreversibly with rising temperature, but it also decreases slowly at a constant temperature above the temperature of deposition. If the surface upon which the film is deposited is of a metal similar to zinc, it influences the temperature resistance relation, but if of a metal not similar to zinc, it does not. The experiments favor the assumption that agglomeration and crystallization are responsible for the changes in resistance.

INTRODUCTION

THE electrical conduction of thin metallic films condensed at low temperature has been often studied in the past, and while this work was in progress many new observations were published which to a great extent agree with ours. Therefore we shall confine ourselves in this paper to the description of results which seem to be new.

The main facts concerning the behavior of these films known hitherto are as follows: Thin films of metals deposited upon a nonconducting surface at the temperature of liquid air show a high resistance, which decreases with rising temperatures, until finally the resistance is of the order of magnitude of that of the normal metal. If such a temperature is reached that the resistance is comparable to that of the normal metal, the cooling of the layer will not again result in a rise of the resistance, but there will be a small decay of the resistance corresponding to the normal positive temperature coefficient of resistance of the bulk metal. According to Zahn and Kramer,[1,2] and Kramer[3–5] and Çelebi[6] the shape of the temperature-resistance curve for all metals is such that the resistance does not change much until a well-defined transition temperature is reached, at which the resistance drops suddenly to normal values. According to other papers, for instance by Suhrmann and his co-workers,[7–10]

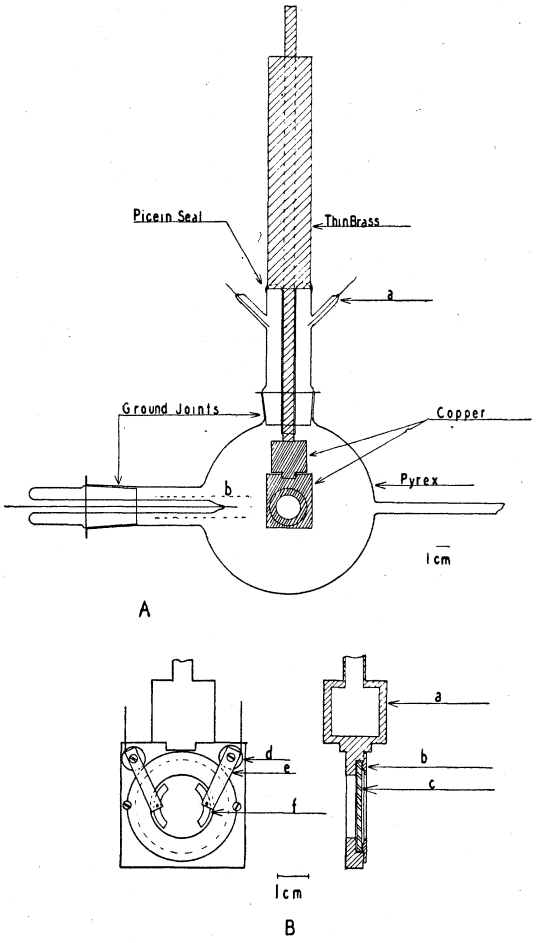

FIG. 1. Diagram of apparatus.

there is with most metals no such transition temperature, but a continuous decay of the resistance with rising temperature. The change of

[1] J. Kramer and H. Zahn, Naturwiss. **20**, 792 (1932).
[2] H. Zahn and J. Kramer, Zeits. f. Physik **86**, 413 (1933).
[3] J. Kramer, Ann. d. Physik **19**, 37 (1934).
[4] J. Kramer, Zeits. f. Physik **106**, 675 (1937).
[5] J. Kramer, Zeits. f. Physik **106**, 692 (1937).
[6] Çelebi, Zeits. f. Physik **106**, 702 (1937).
[7] R. Suhrmann and G. Barth, Physik. Zeits. **35**, 971 (1934).
[8] R. Suhrmann and W. Berndt, Physik. Zeits. **37**, 146 (1936).
[9] R. Suhrmann and G. Barth, Zeits. f. Physik **103**, 133 (1936).
[10] Tadao Fukuroi, Nature **139**, 884 (1937).

resistance of the films from low temperature to the temperature at which the resistance is normal is about 50-fold. On the other hand, there are cases of metals showing Zahn and Kramer's sudden transition. A very well-known example of this is the case of antimony, where for instance, electrolysis produces layers which go over explosively with rising temperature. Kramer got analogous results with sputtered films of antimony, and Suhrmann and his co-workers, and we also, studied antimony deposited by evaporation in high vacuum. At the transition point the resistance changes by a factor of a thousand or more. For such transitions one has to accept Zahn and Kramer's explanation of the transition from a nonmetallic state in which each valence electron belongs to one atom or molecule, to the metallic state. We expect such behavior only with metals which like antimony form saturated molecules by exchange forces, which repel other molecules approaching them. These repulsive forces can form a potential barrier against the transition to the metallic state, if the heat of dissociation of the molecules, and correspondingly the repulsive forces, are large enough. In metals forming monatomic vapors, or molecules only by the van der Waals and Coulomb forces, as for instance mercury and cadmium, the formation of a potential barrier seems unlikely.[11] The much smaller irreversible changes of resistance occurring in the latter cases are, as many authors agree, produced by an agglomeration and crystallization process.[12, 13] The following experiments are in accordance with this hypothesis.

Experimental

The thin metallic films were evaporated in high vacuum ($\sim 10^{-6}$ mm of Hg) and condensed on a

[11] But in papers which have recently appeared Kramer and Kramer and Çelebi, references 4, 5, 6, repeat the statement that all metals show sharply defined transition points if deposited under the right conditions. Compare on the other hand, the discussion at the Conference on the Conduction of Electricity in Solids, at Bristol, Proc. Phys. Soc. **49**, 151 (1937), in which most of the authors seem to come to results comparable to ours.

[12] Georg Hass, Naturwiss. **15**, 232 (1937).

[13] E. N. daC. Andrade and J. G. Martindale, Phil. Trans. Roy. Soc. **235**, 69 (1935).

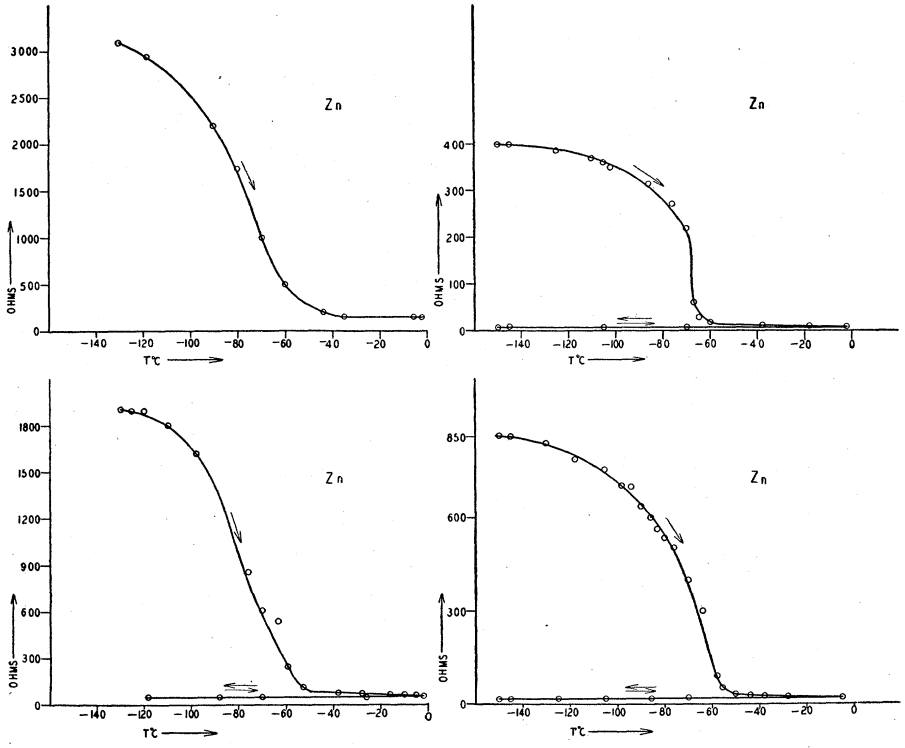

FIG. 2. Resistance of Zn film.

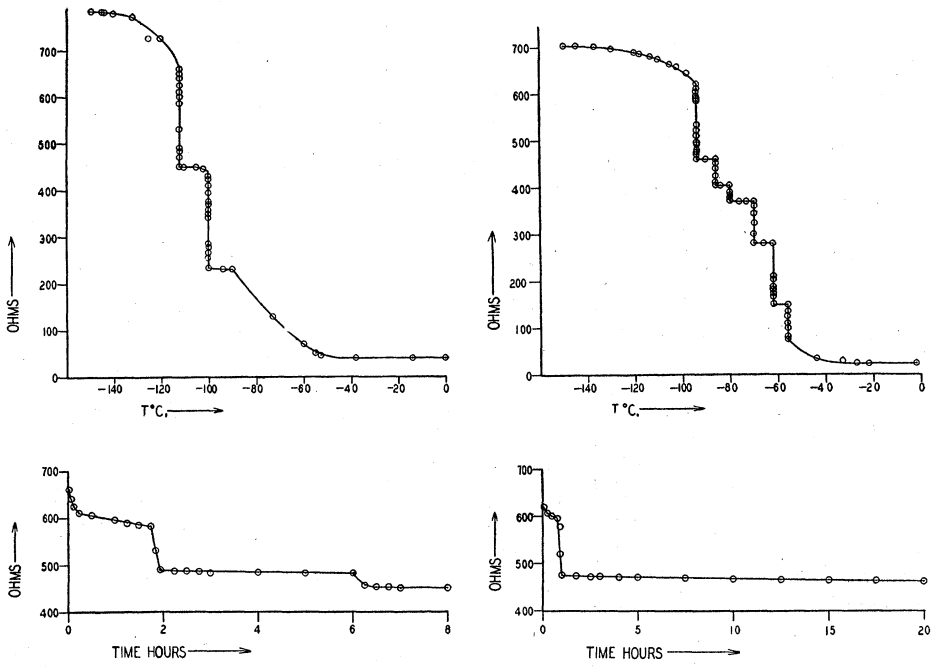

FIG. 3. Resistance of Zn film. Lower curves show change with time.

polished quartz plate cooled with liquid nitrogen. The time of deposition was about 5 minutes. The conductivity was measured in the same vacuum. The apparatus used is shown in Fig. 1. The quartz plate was held in a copper block at the center of the flask (Fig. 1(A)) and leads for the measurement of resistance and temperature were provided. The holder for the quartz plate is shown in detail in Fig. 1(B).

Contact with the films was made by two zones of silver evaporated on the plate in a separate chamber with a clear rectangular strip on the quartz for the metals to be studied. Contact with the silver films was made through spring pressure plates. The temperatures were measured with a thermocouple in contact with the back of the plate. Resistances were measured with a wall galvanometer and source of steady potential for high resistance, and with a Wheatstone bridge for the lower resistances.

RESULTS

The resistance of thin films of zinc has been found, as by other workers[10] to decrease irreversibly with rising temperature (Fig. 2) without a sharp transition point.

However, the resistance also changes with time when the film is held at a constant temperature for a long time. To study this fact, films were condensed at low temperature and the temperature was allowed to rise until the resistance showed a definite decrease, the temperature was then held constant by introducing small amounts of liquid nitrogen or cold gas into the reservoir at frequent intervals. The resistance at first falls rapidly at constant temperature with the time; the fall gradually becoming less rapid until it is nearly zero; after a few hours suddenly another rapid decrease in resistance takes place, followed again by a very slow rate of decrease. The first curve (Fig. 3) shows the result of measurements on one of these films. The curve directly below it shows the change of resistance as a function of time for the first constant temperature part of the curve at $-115°C$. The upper right-hand curve is the result of another run, in which the temperature was held at $-95°C$ for twenty-five hours; the change in resistance for the first twenty hours is shown below this curve. The total time for the second curve was thirty-eight hours. At the end of the first part of the curve the resistance was still decreasing, at a rate that

indicated that it would take about two weeks for the resistance to fall to its final value. As it was not feasible to keep the temperature of the film constant for so long a time, the temperature was raised with the hope that at a slightly higher temperature the resistance would change at a more rapid rate. This it did with each rise in temperature, but the change always became very slow after a few hours at a constant temperature, and it became impractical to hold the film at that temperature for a more extended time. The resistance at no time ceased to decrease in value at a given temperature, however, indicating that if it could be kept at that temperature for a long enough time it would eventually reach its final value at a temperature much below that at which it would usually do so. It would appear then that the change in resistance is not a function of a given temperature, but that the film will change to a condition such that its resistance is normal in behavior at any temperature above that at which it is condensed. A rise in temperature will increase the speed with which this change will take place, and the change will take place with extreme rapidity as the temperature rises, until the condition of normal behavior is reached when no further change occurs. In other words, the resistance can fall below the usual curve, as of Fig. 2; but will not lie above it with rising temperature. It was found that no matter how rapidly the temperature was raised, the resistance would decrease with rising temperature until it reached a value at which it behaved in the normal manner. The resistance temperature curves taken in a comparatively short time, are then only the envelopes of a large number of step-wise curves taken at many temperatures for various lengths of time.

To study the influence of the material on which the layer is deposited, first one layer of zinc was condensed at a low temperature as usual and the temperature raised to about 0°C, the film now behaving in a normal manner, the temperature was again lowered to about −150°C while the resistance was measured at frequent intervals during the cooling. Then a second film was condensed upon the first and the change of resistance of the two films together was measured as the temperature was raised. The resistance of the upper film could be calculated by considering the two films to be resistances in parallel. The change of the resistance thus calculated is shown for two of these films in Fig. 4. The resistance of these films condensed upon normal films drops with lower temperatures and more rapidly with changing temperature than that of the films condensed upon the quartz. In the film whose curve is shown at the right (Fig. 4), the resistance has already fallen nearly to the final value at the temperature at which it was condensed, and the curve flattens out in approaching the normal behavior at much lower temperatures than that of the films deposited upon the quartz. This film was very thin, as shown by the high final resistance.

From this it is seen that the structure of the surface upon which the film is condensed will

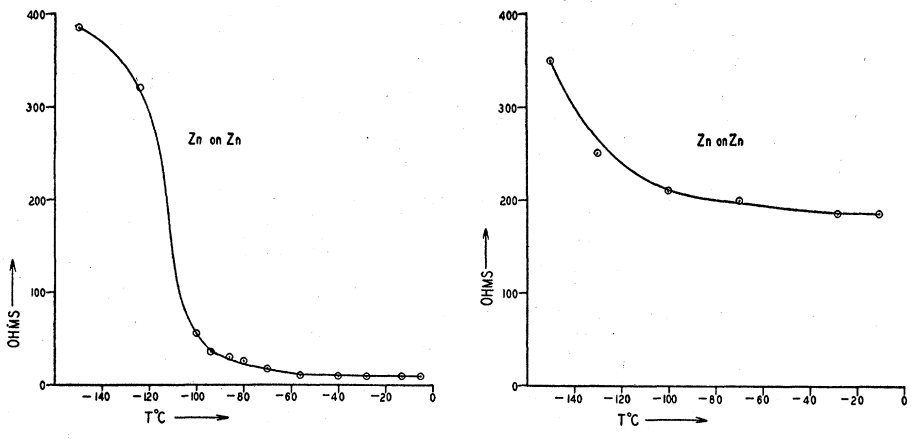

FIG. 4. Resistance of Zn film on a Zn film.

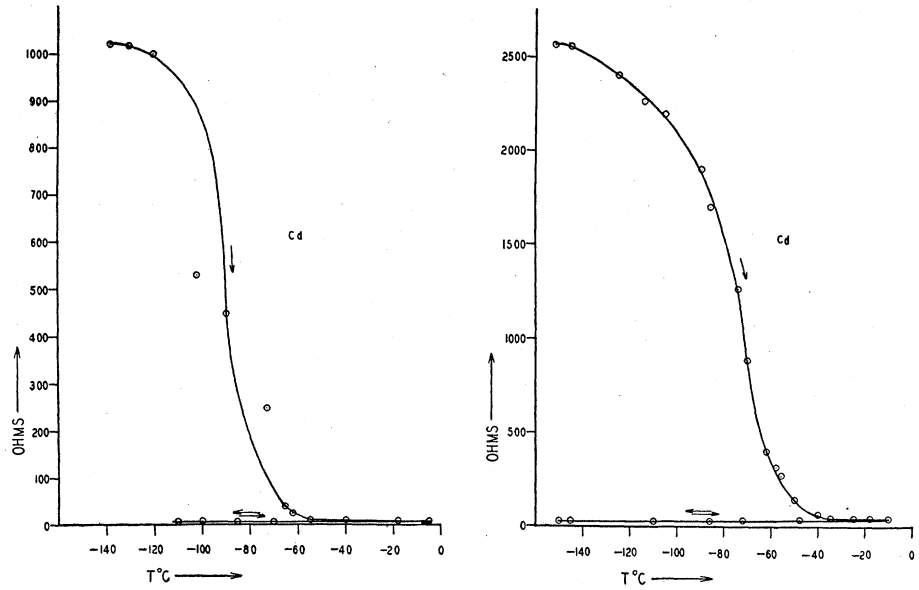

FIG. 5. Resistance of Cd film.

change the temperature at which the film becomes normal in behavior.

Next the influence on the curves of the replacement of the first layer of zinc by another metal was studied. Cadmium was chosen since it has a similar structure to zinc and a low melting point, so that the formation of an alloy at the borderline between the two metals could be expected to a given extent in spite of the low temperatures.

The films of cadmium were condensed at low temperature and their resistance studied at different temperatures. The resistance of cadmium decreases with rising temperature very similarly to that of zinc, except that the effect of different thicknesses is more apparent and the resistance changes by a larger factor than in the case of zinc. The resistance of cadmium changed more rapidly than zinc at low temperatures for thicker films (Fig. 5).

Then the films of cadmium were cooled again to about $-150°C$ and the zinc condensed upon them. The resistance of the two films was measured with rising temperature as with the double films of zinc, and the change in resistance of the upper film of zinc calculated as before. The curve of resistance against temperature for the zinc film upon the cadmium was shifted as in the case of the zinc upon zinc, but to an amount less than in the case of zinc on zinc (Fig. 6). From this it is seen that the structure of the underlying layer influences the temperature at which the zinc film becomes normal in behavior, even though the underlying film is of a metal different from zinc.

It was then desired to find out what effect an underlying film of a metal of different properties would have upon the change in resistance of these zinc films. Since silver has a different crystal form from zinc, a much higher melting point, and different electrical and chemical properties from zinc, it was chosen as an underlying layer. The silver film was prepared in the usual manner and the temperature raised to bring the silver into a normal condition. The silver film was then cooled again, the zinc condensed upon it and the temperature raised. The resistance of the zinc decreased in the usual manner, but there was no shift to lower temperatures as observed with an underlying film of zinc or cadmium. With silver under the zinc films, they behaved in the same way as upon the quartz, (Fig. 7). Apparently a metal of quite different properties has no effect upon the change in resistance of these thin zinc films.

CONCLUSION

From the foregoing results it seems that the following conclusions may be drawn. The change

in these films from a condition of high resistance to one of low resistance with rising temperature is not a transition taking place at a temperature characteristic of the metal. This change occurs more rapidly as the temperature is raised, but will also occur at a constant low temperature, if one waits a long enough time. The curves of Fig. 3 we explain in the following way. There are at first a few small centers of crystallization formed which result in an initial rapid fall of the resistance. This is followed by a gradual growth of crystals about these centers which results in the slow decay of resistance, followed again by a rapid fall of resistance as new centers of crystallization are formed. When the temperature is raised, these centers form more rapidly, and the subsequent growth about them is also more rapid. This behavior would account fully for the results found with the films held at a constant temperature below that at which they usually become normal in behavior.

If the surface under the film is of the same

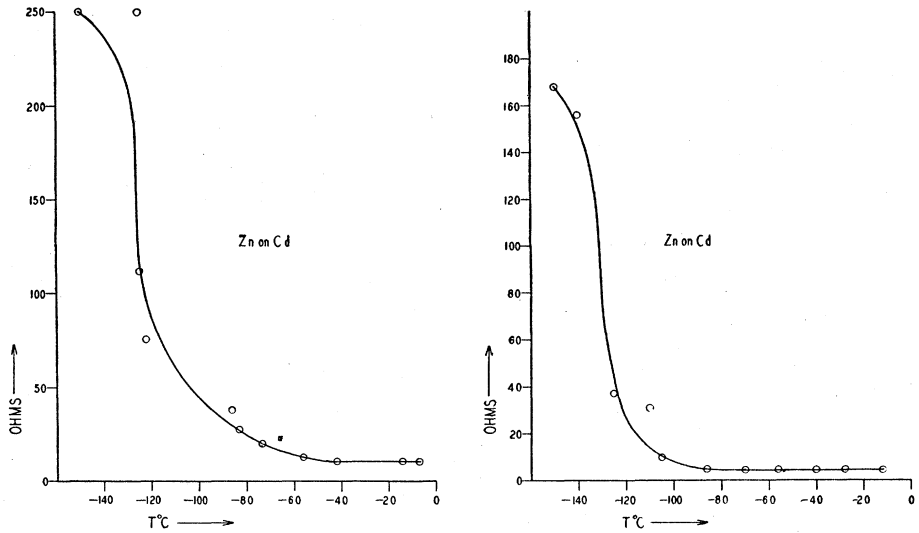

FIG. 6. Resistance of Zn film on Cd film.

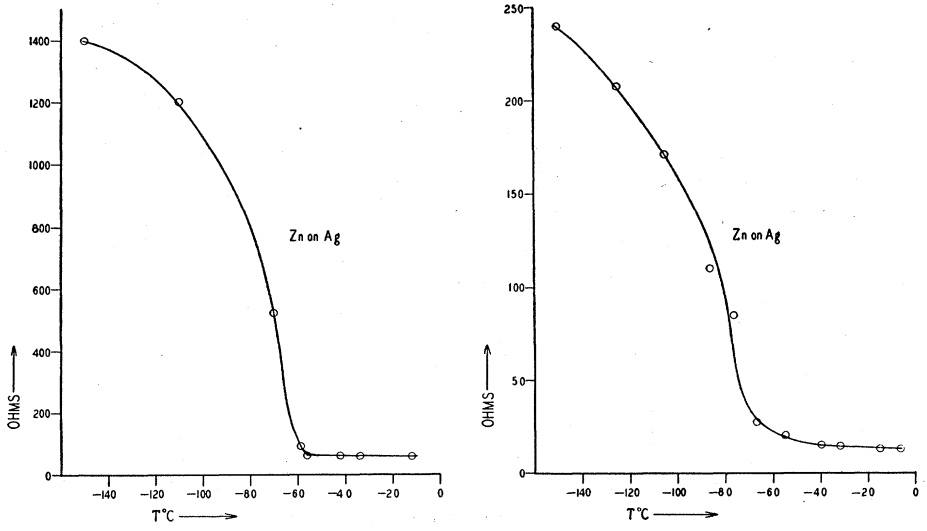

FIG. 7. Resistance of Zn film on Ag film.

metal in a normal condition, or a metal with which the upper film will easily form an alloy at a fairly low temperature, the underlying metal will induce the crystallization and accompanying change to a normal resistance at a lower temperature than when the film is condensed on a quartz surface. If the surface underlying the film is of a metal of quite different properties, the film deposited on it will not form a close association with it and the resistance will change in the same manner as on a nonconductor. This would account for the results as found with the double layer films, represented by Figs. 4, 6, and 7.

I wish to thank Professor Franck for his helpful advice, and Professor Wood, on whose proposal the study of thin films was undertaken, for this suggestion and his cooperation in making special facilities of the laboratory available. I also wish to thank other members of the physics department for their timely help.

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Static Universe and Nebular Red Shift. II

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The geometric foundation and the mathematical consequences of the model of a static universe proposed in a previous paper are discussed. The formula for the gravitational constant is proved and some cosmological applications are pointed out.

1. INTRODUCTION AND BASIC ASSUMPTIONS

IN a previous paper,[1] one of the authors has suggested a model of a static universe with shrinking atomic lengths in order to explain the red shift and nebular distribution observed. Such a model is essentially equivalent to that of a nonstatic universe with constant atomic lengths, but has the added advantage of relating cosmic phenomena such as gravitation, with certain atomic properties. It was suggested that, if the world radius R is considered a constant, Hubble's red shift distance law involves the very gradual shrinking with time of Planck's constant h, as well as of the electron charge. Assuming that the differences between the atomic energy levels remain constant while h diminishes, we deduce that light must have been emitted at a lower frequency the further back in time the emission occurred. It must be emphasized here once more that in describing the propagation of light in space, the wave concept must be used, as pointed out by Laue,[2] since this fits satisfactorily with the general theory of relativity and therefore with any relativistic cosmology. According to the wave theory light traveling on a geodesic zero line reaches us with its frequency unchanged, and therefore permits us to observe a red shift. In this way, the energy principle, which is assumed throughout this theory, remains valid for the propagation of light in space. The consistent application of the concept of light quanta would inevitably lead to difficulties in respect of the energy balance in view of the incompatibility of a rigid adherence to the light quanta concept with the general theory of relativity. The dualism involved in the use of the quantum equation $\Delta E = h\nu$ for the process of emission and the description of the propagation of light in terms of waves is therefore inevitable at the present stage of our knowledge.

In this paper the mathematical foundations of this theory will be considered at greater detail, more particularly with regard to the consequences of the shrinkage of the hydrogen atom. We will begin by considering the behavior of a hydrogen atom in a universe with Weylian metric, the geometry of whose space is given by a quadratic to be more closely defined later, and by a linear differential which introduces the necessary gauge. If this universe is a static one, its constant radius of curvature will provide a standard measure of length for any of its points.

[1] S. Sambursky, Phys. Rev. **52**, 335 (1937).
[2] M. v. Laue, Zeits. f. Astrophys. **12**, 208 (1936).