Size Effects in the Superconductivity of Cadmium

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The magnetic threshold field of superconducting cadmium has been investigated as a function of specimen size. With the exception of the bulk material, the specimens were in the form of spheres. In all, five distinct groups were investigated ranging in size from the bulk specimen (irregularly shaped pieces of dimensions of the order of mm) down to spheres 44–62 microns in diameter. A ballistic mutual inductance technique was employed to detect the superconducting transitions. While all the specimens exhibited the same zero-field transition temperature (T_c), a marked increase in the magnetic threshold fields was observed for the three smallest groups. If this increase in the magnetic threshold curves is interpreted in light of existing theories as being due to the specimen size becoming comparable to the penetration depth, values of $(10.4\pm0.4)\times10^{-4}$ cm and $(8.8\pm0.3)\times10^{-4}$ cm are obtained for λ_0, the penetration depth at absolute zero. These two values for λ_0 are based on theoretical expressions presented by von Laue and Silin, respectively.

INTRODUCTION

THE authors have reported[1] that the magnetic threshold fields of superconducting cadmium spheres 44–62 microns in diameter, were considerably higher than that of the bulk material. This increase in the threshold fields was interpreted in the light of present theories and a value of $\sim10^{-4}$ cm were estimated for λ_0, the penetration depth at absolute zero. This figure, 100 times larger than the values quoted for indium, lead and tin,[2] is based on data obtained using a lead (Pb) thermal switch in the production of temperatures below 1°K. The relatively large value for λ_0, the observed transition temperature of 0.64°K, which is high compared to previously reported values,[3] the relatively fast warmup times (approximately 40 minutes), and the fact that the spheres were embedded directly in the salt pill causes some reservations about the results as well as the interpretation.

Because the concept of the penetration depth plays an important role in all theories of superconductivity, it was felt that a more detailed investigation of the magnetic threshold fields of small superconducting spheres of cadmium would be of interest. With this in mind the equipment was modified to eliminate most of the above objections and the experiments were repeated and extended to other specimens.

SPECIMENS

The cadmium used in this work was spectrographically pure Johnson-Matthey material. The spheres were formed by whipping the molten metal in a bath of hot silicone oil.[4] These spheres were then separated into size groups by means of a mechanical shaker and sieves. The four groups investigated contained spheres with diameters 44–62 microns, 88–105 microns, 125–149 microns, and 600–1200 microns. A microscopic examination revealed that the particles were indeed spherical, with diameters in the ranges as indicated above.

EXPERIMENTAL DETAILS

In general the experimental arrangement was similar to that previously employed.[5] Temperatures below 1°K were produced by the magnetic cooling method using potassium chrome alum as the cooling agent. The large magnetizing fields were supplied by a Bitter-type solenoid, and the exchange gas technique was employed. Thermal contact between the cadmium and the paramagnetic salt was achieved by cementing the specimens into a copper sleeve which in turn was connected, via a screw fitting, to a copper fin around which the paramagnetic salt was compressed. The

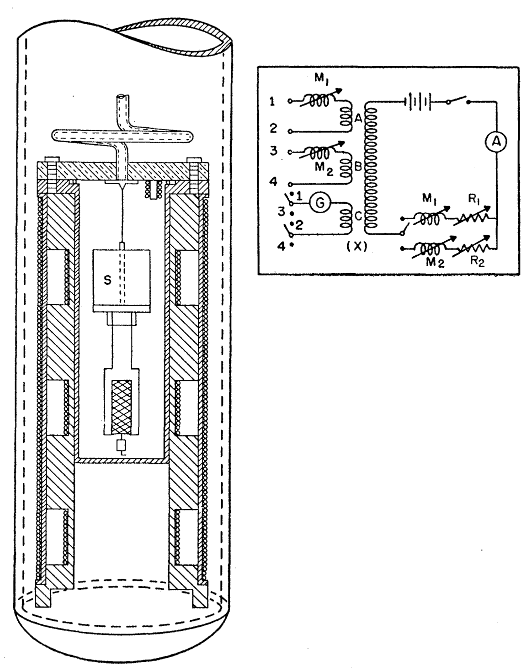

Fig. 1. Schematic diagram of the lower Dewar assembly.

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[1] M. C. Steele and R. A. Hein, Phys. Rev. **87**, 908 (1952).
[2] J. M. Locke, Proc. Roy. Soc. (London) **A208**, 391 (1951).
[3] B. B. Goodman and E. Mendoza, Phil. Mag. 42, 594 (1951).
[4] M. C. Steele, Phys. Rev. **78**, 791 (1950).
[5] M. C. Steele and R. A. Hein, Phys. Rev. **92**, 243 (1953).

TABLE I. Critical field data for all of the cadmium samples.[a]

Bulk specimen		Spheres 600–1200 microns		Spheres 125–149 microns		Spheres 88–105 microns		Spheres 44–62 microns	
H(gauss)	T°K	H(gauss)	T°K	H(gauss)	T°K	H(gauss)	T°K	H(gauss)	T°K
0	0.554	0	0.554	0	0.561	0	0.564	0	0.551
5.6	0.484	8.8	0.441	12.3	0.475	0	0.559	10	0.539
10.8	0.430	15.0	0.375	19.2	0.375	12.5	0.494	22.5	0.486
12.5	0.409	17.5	0.322	25.4	0.304	19.3	0.414	25.0	0.429
16.5	0.349	25.0	0.163	28.6	0.255	20.8	0.389	33.8	0.349
22.5	0.241					21.7	0.389	37.2	0.303
0	0.549					25.5	0.358	33.8	0.352
8.7	0.452					0	0.561	0	0.563
14.9	0.371					8.0	0.518	0	0.548
18.8	0.306					20.5	0.409	12.5	0.528
16.4	0.355					26.8	0.324	25.0	0.438
24.0	0.195							30.8	0.391
								33.6	0.359
								45.0	0.190

[a] The earth's magnetic field was not compensated for in these experiments.

cadmium spheres were cemented into the copper sleeve, by first placing a small amount of G. E. Adhesive No. 7031 and cadmium into it, and then stirring the mixture and allowing it to dry. This procedure was repeated until the sleeve was full. A carbon-composition resistor, calibrated for use as a thermometer, was incorporated into the setup to check on the quality of the thermal contact between the spheres and the salt pill (see Fig. 1). A ballistic mutual inductance technique was employed to detect the superconducting transitions as well as to obtain the magnetic temperature. It should be noted that in the present arrangement, the cadmium samples were separate from the salt pill, and by means of a three-coil secondary, the differential magnetic susceptibility of the salt or of the metal could be independently observed.[6]

The superconducting transitions were obtained by first cooling the specimen to temperatures of the order of 0.1°K and then observing its magnetic behavior as it warmed back to the temperature of the liquid helium bath. The transition temperature is defined as that temperature at which the magnetic susceptibility of the specimen returns to its normal value. Temperatures were calculated from the susceptibility of the salt, which was also observed as the system warmed up. The temperatures so calculated are corrected to that of a spherical sample by applying the usual geometrical correction.[7] The magnetic temperature (T_s^*) was then converted to the thermodynamic temperature.[8] By observing a series of warmups in the presence of small applied magnetic fields, supplied by an auxiliary solenoid wound on the casing of the Bitter magnet, the transition temperatures were obtained as a function of the applied magnetic field. A plot of this dependence constitutes the magnetic threshold field curve for the particular specimen under investigation.

[6] R. A. Hein, Phys. Rev. **102**, 1511 (1956).
[7] N. Kurti and F. Simon, Phil. Mag. **26**, 849 (1938).
[8] B. Bleaney, Proc. Roy. Soc. (London) **208**, 216 (1950).

RESULTS

The magnetic threshold fields obtained for the specimens are presented in Table I and plotted in Fig. 2. The zero-field transition temperature (T_c) of all the samples was found to be 0.555±0.010°K, a value which is in accord with the findings of earlier workers.[3] The critical field curve of the bulk material was parabolic and could be represented by

$$H=27.6[1-(T/0.555)^2].$$

While the magnetic threshold fields of the 600–1200 micron spheres were in accord with the bulk behavior, the data obtained for the three smallest specimens indicate a definite increase in their critical magnetic fields. The critical field curves of these specimens could not be represented by any parabolic relationship. The increase in the threshold fields is presented somewhat differently in Fig. 3, where the ratio of the critical

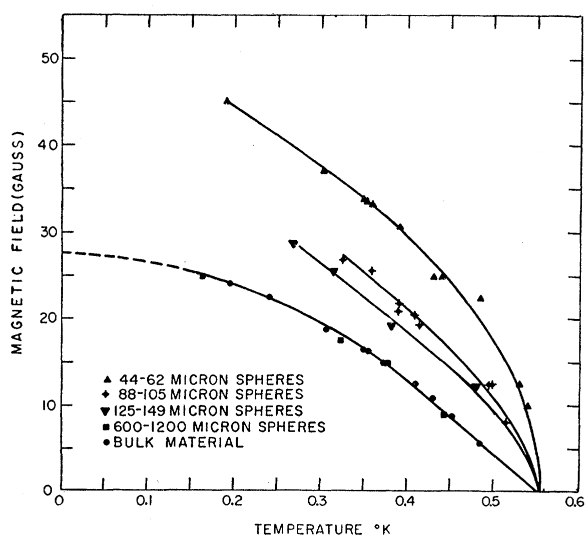

FIG. 2. The critical magnetic fields of all the specimens as a function of the absolute temperature.

field (H_{cs}) of the particles to that of bulk material (H_{cL}) is plotted as a function of the reduced temperature, $t=T/T_c$. These ratios were obtained by comparing the measured critical fields of the spheres, with the appropriate field for the bulk material calculated from the above expression. These curves show that this ratio increases rapidly as the temperature approaches the transition temperature and tends to level off as the temperature approaches zero.

Two runs were performed with spheres having diameters in the 20–30 micron range. The data obtained, (because of poor thermal contact between the spheres and the salt) were felt to be unreliable and therefore not included. Lack of intimate thermal contact was evidenced by the fact that the spheres did not go superconducting until thirty minutes after the magnetizing field had been reduced to zero although the salt itself cooled to a temperature (T_s^*) of 0.031°K. At thirty minutes after demagnetization the temperature of the salt was 0.177°K, indicating the presence of a relatively high thermal gradient between the spheres and the salt. Due to the small quantity of material available, no carbon resistor was incorporated in these experiments. These results suggest that the technique using to provide thermal contact is limited in its application.

DISCUSSION OF RESULTS

Present theories predict curves similar to those of Fig. 3 for superconductors whose dimensions are

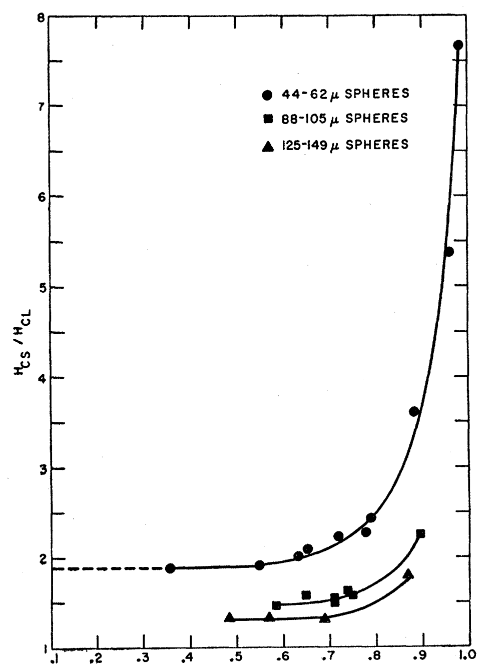

FIG. 3. The reduced critical magnetic fields of the 44–62 micron, 88–105 micron and 125–149 micron spheres as a function of the reduced temperature.

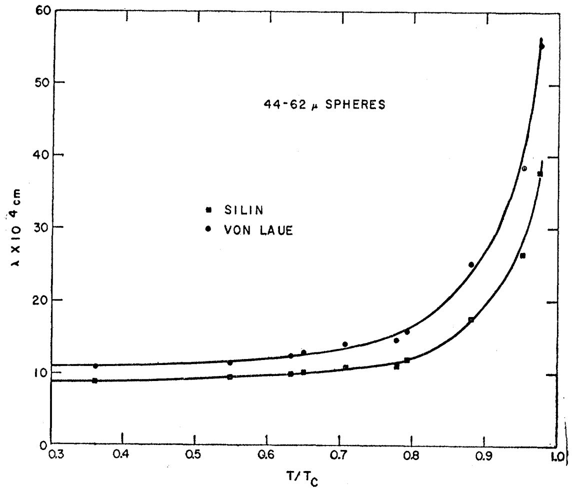

FIG. 4. The penetration depth calculated from the 44–62 micron sphere data as a function of the reduced temperature.

comparable to the penetration depth. Calculations by von Laue[9] and de Launay,[10] based on the London theory, show that the ratio of H_{cs} (critical field of small spheres) to H_{cL} (critical field of large spheres) is given by

$$\frac{H_{cs}}{H_{cL}}=\sinh(R/\lambda)\Big/\left(\cosh(R/\lambda)-\frac{\sinh(R/\lambda)}{R/\lambda}\right),$$

where R is the radius of the sphere and λ is the penetration depth. Since the ratio H_{cs}/H_{cL} is temperature-dependent, a plot of this expression as a function of R/λ, in conjunction with the curves of Fig. 3, allows one to determine λ as a function of the temperature, provided R is known. An extrapolation of the 44–62 micron sphere curve in Fig. 3, yields a value of 1.85 ± 0.05 for the ratio of H_{cs}/H_{cL} at absolute zero of temperature. Using the above expression, a value of $(10.4\pm0.4)\times10^{-4}$ cm is obtained for λ_0, the penetration depth at absolute zero. This analysis assumes that the measured critical fields are characteristic of the smallest particles present to any appreciable extent; i.e., 44 micron diameter spheres in the present case. A similar calculation by Silin,[11] based on the theory of Ginsberg and Landau, which takes into account surface energies, shows that the ratio of the critical fields is given by

$$H_{cs}/H_{cL}=(2\sqrt{5})(\lambda/R).$$

This expression, and the curves in Fig. 3, also allow one to obtain λ as a function of the temperature, and gives a value of 8.8×10^{-4} cm for λ_0.

An independent check on the magnitude of λ_0, can be obtained from the work of Pippard[12] in which he

[9] M. von Laue, *Theory of Superconductivity* (Academic Press, Inc., New York, 1952), p. 114.
[10] J. de Launay, Naval Research Laboratory Progress Report, Oct. 1947 (unpublished), p. 14.
[11] V. P. Silin, J. Exptl. Theoret. Phys. **21**, 1330 (1951).
[12] A. B. Pippard, Phil. Mag. **43**, 273 (1952).

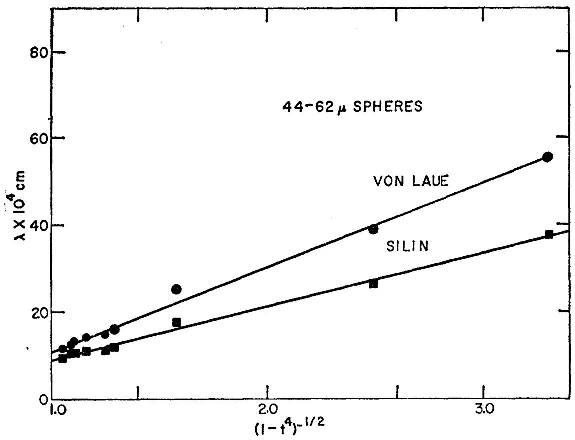

FIG. 5. The penetration depth calculated from the 44–62 micron sphere data as a function of $[1-(T/T_c)^4]^{-\frac{1}{2}}$.

presents expressions for the reduced critical field curves of small superconducting spheres. The data obtained for the 44–62 micron spheres approximate his expressions for a sphere of radius $2\lambda_0$. Hence, λ_0 is approximately 11×10^{-4} cm from this analysis.

A plot of the penetration depth (λ) as a function of temperature, obtained using the above expressions, see Fig. 4, displays the usual characteristics. That is, as the temperature approaches the transition temperature, λ becomes quite large while as the temperature approaches the absolute zero λ tends to level off and become constant. There exists a theoretical expression, due to Daunt,[13] for the temperature dependence of the penetration depth which can be written as

$$\lambda=\lambda_0[1-(T/T_c)^4]^{-\frac{1}{2}}.$$

This relationship has been used to estimate values for λ_0, from data obtained near T_c.[14] Clearly, if one plots λ as a function of $[1-(T/T_c)^4]^{-\frac{1}{2}}$, this expression yields a straight line with a slope and an intercept at $T=0$ of λ_0. A plot of the values of λ obtained from the 44–62 micron sphere data is presented in Fig. 5. While the data are seen to display a linear behavior, the intercept and slope do not yield the same value for λ_0. The intercepts of 10.8×10^{-4} cm and 9.0×10^{-4} cm are in accord with the values obtained by extrapolating the curve in Fig. 3. The slopes of 19.5×10^{-4} cm obtained by using von Laue's analysis and 12.8×10^{-4} cm by using Silin's, are too large for agreement with the values plotted in Fig. 4. Therefore, the curves in Fig. 4 show that the values of λ calculated on the basis of von Laue's or Silin's analysis are inconsistent with the T^4 behavior.

In an attempt to ascertain if this discrepancy between slope and intercept is a consequence of the particular value assigned to the radii of the spheres used in the calculation of λ, additional values of λ were determined with values of 25 and 30 microns for the radii of the spheres. The results, when plotted against $(1-t^4)^{-\frac{1}{2}}$, where $t=T/T_c$, again displayed a linear behavior, but the slope and intercept were still in disagreement. The results are tabulated in Table II.

There is another point of interest and that is that the data, again using either von Laue's or Silin's analysis, indicate a dependence of λ on the specimen size. Although the data for the 88–105 micron and 125–149 micron diameter spheres are somewhat meager, the calculated values for λ tend to increase with an increase in particle size. This dependence is depicted in Fig. 6. The curves here, obtained using von Laue's expression, suggest that as the temperature approaches the transition temperature λ becomes independent of particle size, while at lower temperatures the smaller particles give the smaller penetration depth.

Because of the relatively large values for λ_0, these experiments should be carefully scrutinized. The carbon resistor indicated that the equilibrium times in the initial cooling down, after a demagnetization, were of the order of five minutes or less. Since the warmup times were usually longer than two hours, it is unlikely that the systematic spread in the threshold field curves was due to errors in the temperature resulting from poor thermal contact. To check on the possibility of errors in the calibration of the salt, which serves as the magnetic thermometer, or error due to the position of the specimen in the field of the auxiliary solenoid, a series of demagnetizations were conducted using a composite sample containing bulk cadmium as well as some 44–62 micron spheres. The bulk cadmium used here were irregular shaped pieces (dimensions of the order of mm) which were recovered from the same silicon oil bath as were the spheres. The reasoning behind this experiment may be readily seen with reference to Fig. 2. It should be noted there that if the composite is cooled to temperatures below 0.55°K, a subsequent warmup in zero field should yield a single transition in the neighborhood of 0.55°K. However, a warmup in the presence of an applied magnetic field, should, if the spread in threshold fields is real, yield a double transition—the first for the bulk material and the second at a higher temperature for the 44–62 micron spheres. A double transition should also be

TABLE II. Intercepts and slopes obtained from $\lambda=\lambda_0[1-t^4]^{-\frac{1}{2}}$ for values of λ calculated by using the indicated values for the radii of the spheres.

Radii of spheres $\times10^4$ (cm)	von Laue intercept ($T=0$) $\times10^4$ (cm)	Slope $\times10^4$ (cm)	Silin intercept ($T=0$) $\times10^4$ (cm)	Slope $\times10^4$ (cm)
22.0	10.8	19.5	9.0	12.8
25.0	11.6	23.4	10.0	14.5
30.0	13.8	26.2	11.6	15.6

[13] J. G. Daunt *et al.*, Phys. Rev. **74**, 842 (1948).
[14] D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), Chap. V.

observed by making a magnetic field sweep, at temperatures below the transition temperatures.

Figures 7 and 8 show the results obtained with the composite sample. The zero-field transition is similar to the zero-field transition obtained with the bulk material and indicates a single transition at 0.0558°K. The transition in a field of 10 gauss, see Fig. 8, is markedly different from the zero-field one in that two transitions are evident. The first transition (lower temperature) agrees well with the bulk critical field curve while the second transition (higher temperature) is in keeping with the 44–62 micron spheres critical field curve. The curves in Figs. 7 and 8 show definitely that the spread in threshold fields is real. A field sweep conducted at approximately 0.25°K also revealed a double transition.

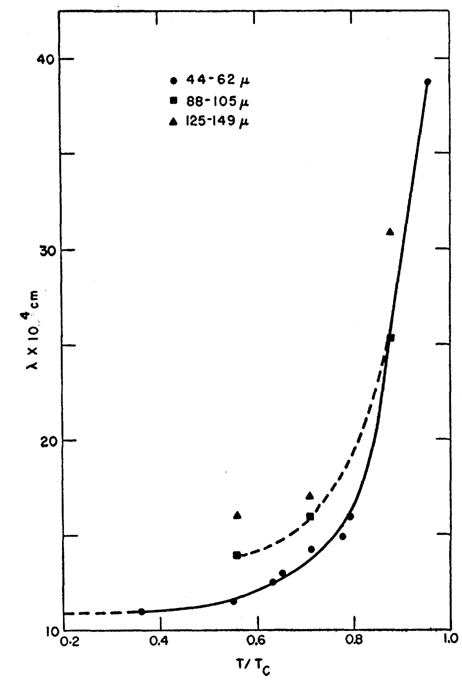

FIG. 6. The penetration depth calculated from all the data as a function of the reduced temperature.

To check further on the experimental technique, a composite tin sample, consisting of bulk material and 44–62 micron spheres, was investigated in the liquid helium range. These spheres were made in the same manner as were the cadmium spheres and the experimental arrangement was the same. Several field sweeps conducted at approximately 2.0°K indicated but a single superconducting transition. This result is in keeping with what one would expect, since λ_0 for tin[2] is known to be about 5×10^{-6} cm so that the radii of the spheres were approximately 400 times λ_0. Therefore, the absence of a double transition is consistent with the interpretation put on the cadmium data.

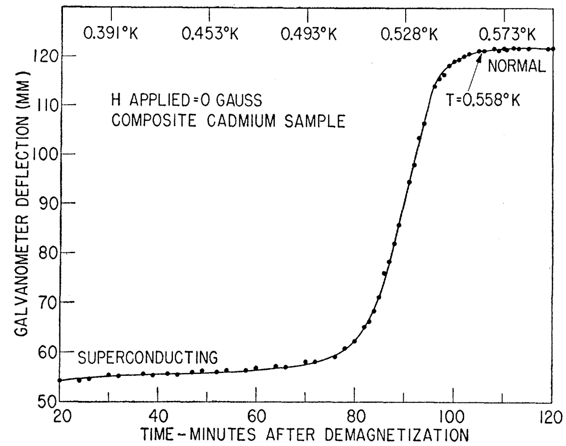

FIG. 7. The galvanometer deflection obtained in zero applied magnetic field for the composite cadmium sample as a function of the time after demagnetization.

CONCLUSIONS

From the results of the present investigation, it is concluded that the spread in the critical field for the small superconducting spheres of cadmium is real and a property of the spheres themselves. The values of $(10.4\pm4)\times10^{-4}$ cm and $(8.8\pm0.3)\times10^{-4}$ cm for λ_0 is in qualitative agreement with the empirical observations[2] and theoretical predictions[15] that the penetration depth varies inversely with the transition temperature. These results and the results of our earlier work strongly suggest that λ_0 for cadmium is a factor of 100 times larger than the values reported for other superconductors.[14]

This large value for λ_0 suggests that a Casimir-type experiment,[16] in which one measures the change in the volume susceptibility of a bulk superconductor as its

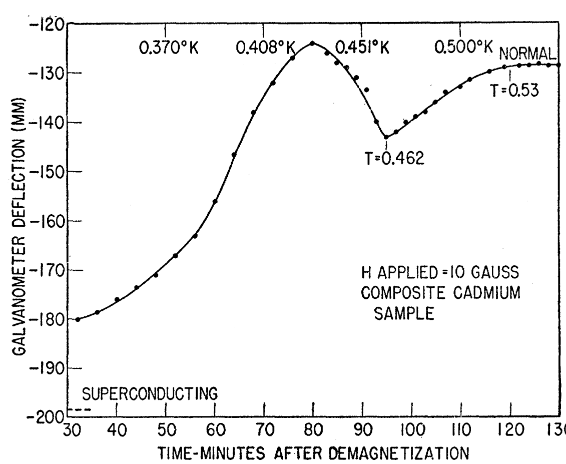

FIG. 8. The galvanometer deflection obtained in an applied magnetic field of 10 gauss for the composite cadmium sample as a function of the time after demagnetization.

[15] M. C. Steele and M. F. M. Osborne, Phys. Rev. **91**, 1281 (1953).
[16] H. B. G. Casimir, Physica **7**, 887 (1940).

temperature is decreased, should be feasible for cadmium. The change in the susceptibility being due to the fact that λ decreases rapidly with decreasing temperature in the region near T_c. It would also appear that resistance measurements on thin cadmium wires might give additional information on the penetration depth. In light of the large λ_0, wires with diameters in the 5 to 10 micron range should produce a readily measurable effect.

ACKNOWLEDGMENTS

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Optical Absorption by Silver Halides*

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The absorption spectra of silver chloride, silver bromide, and silver iodide films evaporated on quartz plates have been measured at room temperature and liquid nitrogen temperature. It has been found that the "exciton peaks," which have been believed to depend very little upon temperature, become sharper and shift toward the shorter wavelength side as the films are cooled down to liquid nitrogen temperature. Attempts are made to combine the present data with some published data to give absorption curves for silver chloride and silver bromide over a large range of absorption spectrum at room and low temperatures.

In the course of our attempts to produce V centers in silver halides by simultaneous evaporation of the silver halide and a halogen gas, we found it necessary to investigate absorption coefficients of evaporated thin films of pure silver halides at room and liquid nitrogen temperatures. It has been generally believed that the absorption bands of the silver halides depend very little upon temperature.[1] In particular, it has appeared that the absorption edge does not shift markedly upon cooling from room temperature, and that the small bumps on the absorption curves, frequently called the "exciton peaks," do not sharpen or grow more pronounced upon cooling. These beliefs have been the basis for various ideas and speculations regarding the energy band structure and absorption mechanisms in the silver halides. The results of our measurements are somewhat at variance with the older data.

Figure 1 shows the results for AgCl. Curve 1 gives the optical absorption coefficient *versus* wavelength for AgCl at room temperature. Curve 2 gives the optical absorption at $-184°C$ and shows that the "exciton" band sharpens and shifts toward the shorter wavelength side at low temperature. These measurements are taken on a thin (210-mμ) AgCl film evaporated onto a quartz plate held at room temperature. Milliman[2] measured the optical absorption of AgCl at room temperature, using thin samples solidified from the melted materials; Curve 3 shows his result. It is noticed that Curve 1 is in fair agreement with Milliman's curve, Curve 3. Curve

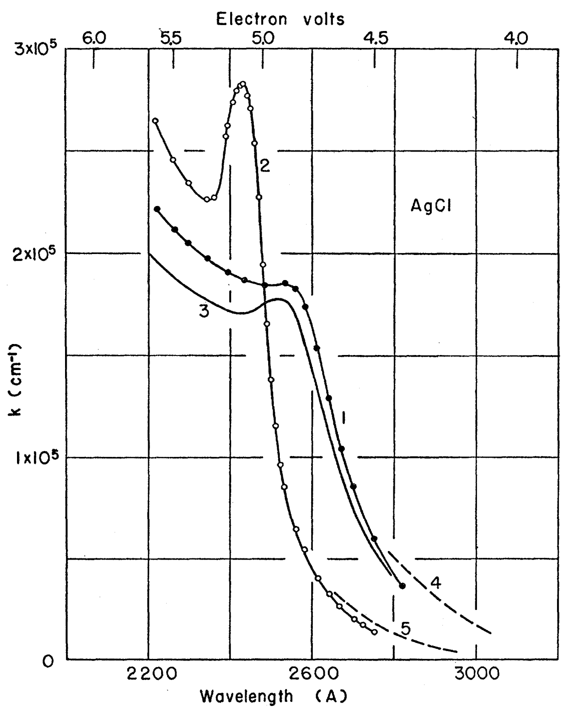

Fig. 1. The absorption spectrum of AgCl at room temperature and liquid nitrogen temperature. Curve 1 is the absorption curve at 26°C, and Curve 2 is at $-184°C$. The measurements were taken on a thin (210-mμ) evaporated film. Curve 3 shows the absorption curve measured by Milliman at room temperature on fused films. Curves 4 and 5 are data measured by Kaiser on an evaporated film of 510-mμ thickness at 27°C and at $-183°C$, respectively.

* This research was supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command.
[1] H. Fesefeldt, Z. Physik **64**, 741 (1930).
[2] P. D. Milliman, Master's thesis, Cornell University, Ithaca, New York, 1954 (unpublished).