

Letters to the Editor

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A New Model for the Debye Dispersion Equations

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THE results of a theory of space-charge polarization effects in materials containing free charges which are blocked at the electrodes¹ indicate that under certain conditions the space-charge contribution to the parallel capacitance and conductance may depend on frequency according to the Debye dielectric dispersion equations. When this is the case, the equivalent series values of capacitance and conductance are frequency-independent. This result suggests that considerable experimental data on dielectric dispersion with a single relaxation time may be due to space-charge effects. Further, most models which lead to the Debye dispersion equations require that the maximum addition to the dielectric constant arising from the dispersion mechanism ($\epsilon_0' - \epsilon_\infty'$) be small compared to unity. This condition is often not satisfied experimentally and is not required in connection with the space-charge model.

The theory yields Debye type frequency dependence when the medium contains (a) charges of only one sign mobile or (b) charges of both signs mobile with the same mobility. In these cases, the results may be expressed in terms of the rms Debye length $L_D = (2D\tau_D)^{1/2}$, where D is the diffusion coefficient for free charges and τ_D is the dielectric relaxation time. If ϵ is the dielectric constant of the material in the absence of free charges and σ_∞ the high-frequency limiting conductivity with charges present, τ_D is $\epsilon/4\pi\sigma_\infty$. It turns out that the frequency-independent series capacitance/cm² arising from space charge C_0 is $\epsilon/4\pi\alpha L_D$ as long as $L_D \ll L$, where L is the separation between plane parallel electrodes. The numeric α is unity for case (a) small dissociation and rapid recombination and is $\sqrt{2}$ for case (a) complete dissociation and for case (b) any degree of dissociation. C_0 is thus formed from the geometrical capacitance/cm² $C_0 = \epsilon/4\pi L$ by merely replacing L by αL_D . In the approximation for which these results are valid, the space-charge series capacitance will be much larger than the geometrical capacitance of the material. The series conductance/cm² in both cases is the ordinary ohmic value $G_\infty = \sigma_\infty/L$. The relaxation time τ_m appearing in the Debye dispersion equations is the time constant of C_0 and G_∞ and is given by $C_0/G_\infty = \tau_D(L/\alpha L_D)$. In this approximation, it is inversely proportional to the square root of the average free charge density and is proportional to electrode separation. As an illustration of typical orders of magnitude for L_D and τ_D , one finds for $\epsilon=5$, $\alpha=1$, and carrier concentration $5 \times 10^{14}/\text{cm}^3$, $L_D = 1.7 \times 10^{-5}$ cm. If, in addition, a mobility of 10 cm²/volt-sec is assumed, $\tau_D = 5.5 \times 10^{-10}$ second.

It is suggested that the results of this space-charge theory may be used to interpret dispersion phenomena in the following physical situations: (a) electrolytes containing positive and negative ions of equal or considerably different mobilities, (b) intrinsic or impurity dominated semiconductors, and (c) photoconductors with blocking electrodes. In case (a), the present theory represents a generalization to nonzero frequencies of older theories of the double layer. The frequency-independent space-charge capacitance in series with the ohmic conductance of the electrolyte

predicted by the present work has been observed by Grahame² and others using ideal polarized electrodes.

Debye type dispersion in selenium rectifiers has been observed by Yamaguchi, Miyauchi, and Mori³ who found a relaxation time τ_m of the order of a microsecond. Insufficient data are presented to allow the present formulas to be applied, but the work of Jaffé⁴ on the same material makes it likely that the dispersion arises from the motion of impurity ions which cannot leave the material through the electrodes. Measurements on photoconducting alkali halide single crystals⁵ have shown that illumination may increase the low-frequency capacitance of the crystals by as much as a factor of 50. This effect arises from free electrons which cannot pass from the crystal to the metallic electrodes at room temperature because of the Fermi-energy conduction-band-energy difference. Finally, measurements by Garlick⁶ and others on photoconducting polycrystalline phosphors show that Debye dispersion is sometimes obtained together with a maximum increase in capacitance of about a factor of two. De Groot⁷ first suggested that this effect may be due to conduction band electrons. The present theory may be expected to apply roughly to the individual crystallites if electrons cannot pass freely from one to another. Because of the high light absorption in polycrystalline phosphors and the fact that the crystallites are in series, one would not expect as large an increase in over-all capacitance as is found in single crystals. A recent phenomenological interpretation along these lines of measurements on photoconducting polycrystalline phosphors has been given by Kallman, Kramer, and Perlmutter.⁸

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- ⁵ J. R. Macdonald, Phys. Rev. **85**, 381 (1952); **90**, 364 (1953).
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- ⁷ W. De Groot, Physica **12**, 402 (1946).
- ⁸ Kallman, Kramer, and Perlmutter, Phys. Rev. **89**, 700 (1953).

Magnetic Refrigerator for Maintaining Temperatures below 1°K*

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IN 1949 two of us (J.G.D. and C.V.H.) proposed¹ a technique for the realization of continuous refrigeration at temperatures well below 1°K. This proposal considered a heat engine in which the working substance was a paramagnetic salt and in which the heat "valves" were constructed of superconducting metallic links.²

The successful operation of such valves was assured from previous observations by us³ of the heat conductivity of pure superconducting Sn and Ta at temperatures well below 1°K and by the actual use of such valves in magnetic cooling experiments.^{3,4} We had found³ that at temperatures below 1°K, which were for Sn and Ta well below the superconducting transition temperatures, the ratio, K_n/K_s , of the thermal conductivity in the normal state to that in the superconducting state could become very large (of order of magnitude 100:1). Hence the same metallic link, depending on whether it was in the normal or superconductive state, would either pass a heat current easily or act essentially as a thermal insulating stop. This valve-like action needed as control of its opening or closing only the application or removal of a small magnetic field greater than the critical magnetic threshold field at the temperature of operation. Such valves, using Pb as the active material, were subsequently further used below 1°K both by Rollin and co-workers,⁵ and by us^{6,7} in two-stage cascade demagnetization experiments, and by Steele and Hein.⁸

We have therefore constructed and have had in operation for some time a continuous refrigerating engine (using Pb for the valves) and in preliminary tests temperatures as low as 0.3°K

have been continuously maintained for long periods with heat extraction rates up about 2×10^4 ergs/cycle and with cycle periods as small as two minutes. The tests have shown the accuracy of the detailed theoretical computations of the performance of the engine presented by two of us some time previously.⁹

The apparatus shown in Fig. 1 consists of 15 g of potassium chromium alum as the working substance, suspended in a vacuum chamber which is immersed in a liquid helium bath at about 1°K. The working substance (upper salt) is connected on the one hand to the bath via a Pb thermal "valve" V_1 which is in the form of a thin ribbon, and, on the other hand, via a similar Pb valve V_2 to the refrigerated reservoir R . In our preliminary experiments the reservoir has been a paramagnetic salt sample identical with the working substance of the engine.

The cycle of operations is as follows (see also reference 1): first the working substance B is magnetized in a field of 9500 gauss with the upper "valve" V_1 to the helium bath "open" so that the heat of magnetization is conducted to the bath. The lower valve V_2 is closed. Before demagnetization of the paramagnetic salt (working substance) the upper valve V_1 is "closed" and on demagnetization the salt B cools. The lower valve V_2 is then opened and the working substance and the reservoir R equalize temperatures. This completes the cycle. To repeat the cycle the lower valve is closed, the upper opened, and then the above operations repeated. The lower Pb valve is controlled by a small air core solenoid producing a magnetic field of 1200 gauss. The upper is controlled by the stray field of the main electromagnet.

In Fig. 2 we show the temperature of the reservoir (and of the bath) as a function of time in a typical run extending for 64 successive cycles. From minutes 5 to 21 the cycle periods were two min, whereas from minutes 40 to 72 the cycle periods were three min. More recent experiments using iron ammonium alum as the working substance and better salt to metal contact have shown greater efficiency and ease of operation.

It is proposed to publish complete details of the construction and operation elsewhere. Our plans for its future use include the establishment of a visible bath of liquid helium down to 0.2°K, the establishment of a more favorable initial temperature platform for magnetic cooling processes; and the establishment of an iso-

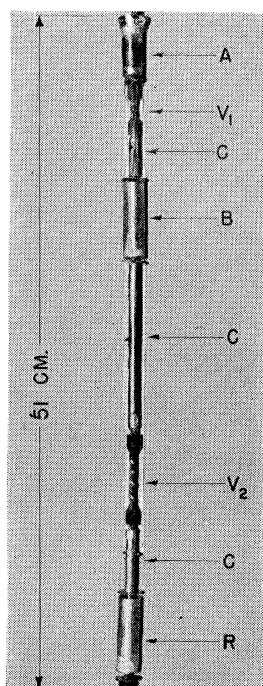


FIG. 1. Photograph of refrigerator and reservoir removed from its vacuum case. The over-all length is 51 cm. A is the anchor to the liquid helium bath at about 1°K, B is the working substance (upper salt), C are carbon resistance thermometers, V_1 and V_2 are the valves, and R is the low-temperature reservoir.

thermal enclosure at about 0.2°K for experiments on nuclear paramagnetism.

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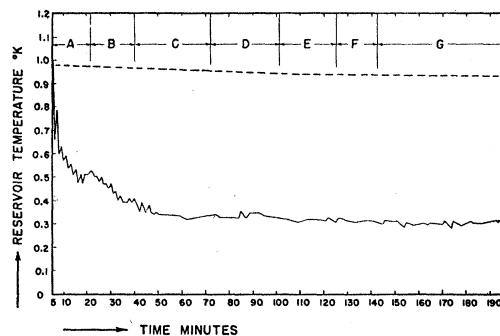


FIG. 2. Plot of typical run extending for 64 cycles. The full curve gives the reservoir temperature. The regions A, B, \dots, G involve different values of the cycling variables, data for which are given in the table below.

Region	Initial magnetic field on B gauss	Final magnetic field on B gauss	Time of magnetization min	Time valve V_2 was open min
A	9500	1500	1	1
B	9500	600	1	1
C	9500	600	1	2
D	9500	385	1	2
E	9500	385	1	2
F	9500	285	1	2
G	9500	220	1	2

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² The use of superconductors as thermal valves was independently suggested by C. J. Gorter [*Les Phénomènes Cryomagnétiques* (Paris, 1948), p. 76], by K. Mendelsohn and J. L. Olsen (Proc. Phys. Soc. **A63**, 1182, 1950) and by us (reference 3).

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Superconducting Compounds

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IN previous notes^{1,2} it had been shown how the nonsuperconducting transition elements form superconducting compounds with semiconductors. The Co, Rh, Ir column has now been completed by establishing superconductivity in Rh_3Ge_2 at 2.12°K,³ thus lying between $CoSi_2$ (1.3°) and IrGe (4.7°).

The element following rhodium in the periodic system is palladium, and the superconducting PdTe and PdSb have already been mentioned.² In addition to these, $\alpha PdBi_2$ and PdBi become superconducting at 3.42° and 3.74°. Alekseevskij⁴ reported recently the transition temperature for $PdBi_2$ at 1.75°. $\alpha PdBi_2$ and PdBi seem to be the first superconducting compounds crystallizing in a monoclinic system.⁵

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³ The structure of Rh_3Ge_2 will be described shortly by Seymour Geller.

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⁵ S. V. Burr and M. A. Peacock, Univ. Toronto Studies, Geol. Ser. No. **47**, 19 (1942).

FIG. 1. Photograph of refrigerator and reservoir removed from its vacuum case. The over-all length is 51 cm. *A* is the anchor to the liquid helium bath at about 1°K. *B* is the working substance (upper salt). *C* are carbon resistance thermometers, *V*₁ and *V*₂ are the valves, and *R* is the low-temperature reservoir.

