Effect of Fluxoid Quantization on Transitions of Superconducting Films*

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This paper presents an elementary theory for the transition of a superconducting film in the presence of a perpendicular magnetic field. The theory is based on the Ginzburg-Landau theory, with emphasis on the qualitatively important consequences of fluxoid quantization. The theory predicts that the transition occurs at a field $H_T(T)=4\pi\lambda_e^2(T)H_{cb}^2(T)/\varphi_0$, where $\lambda_e(T)$ and $H_{cb}(T)$ are the usual penetration depth and bulk critical fields, respectively, and φ_0 is the flux quantum $hc/2e$. Experimental data agree very well with this result if the transition is determined by measuring thermal conductivity or flux penetration. The resistive critical field for full normal resistance appears to be about twice this value, probably because of a residual filamentary structure. The theory also predicts that the angular dependence of the transition field should be given by $(H_T\sin\theta/H_{T\perp})+(H_T\cos\theta/H_{T\parallel})^2=1$. This unusual form agrees with the thermal conductivity measurements of Morris.

The same theory leads in an elementary way to a quantitative interpretation of the periodic variation of T_c with flux through a cylinder in the experiments of Little and Parks. The result for the maximum change is $\Delta T_c/T_c=\varphi_0^2/[32\pi^2R^2\lambda_e^2(0)H_{cb}^2(0)]$. This agrees with their experimental value if $\lambda_e(0)=4700$ Å, whereas from the limited mean free path in the sample one would estimate $\lambda_e(0)\approx 2000$ Å. The agreement is probably within the uncertainties as to the details of the transition region. It should be noted that the present theory predicts a change larger by a factor of order $(T_F/T_c)(l/\xi_0)$ than the theory given by Little and Parks. The present theory also gives a semiquantitative account of the parabolic background effect observed by Little and Parks.

I. INTRODUCTION

IT is well known[1] that the transition of a soft superconductor to the normal state occurs when the magnetic energy resulting from the diamagnetic flux exclusion overcomes the condensation energy of the superconducting state. For bulk superconductors in geometries which eliminate demagnetizing effects (i.e., field parallel to long dimension), this leads to the thermodynamic critical field H_{cb} given by

$$F_n(T)-F_s(T)=H_{cb}^2/8\pi, \tag{1}$$

where F_n and F_s are the free energies of normal and superconducting state, respectively. It is also well known that when one considers a film of thickness comparable to the penetration depth, the critical field H_T at which the transition to the normal state occurs is increased above H_{cb}, provided the field is applied parallel to the surface. This occurs because with the incomplete flux exclusion of a thin film, the magnetic energy is less for a given field. According to the Ginzburg-Landau theory,[2,3] this transition field for a thin film is

$$H_{T\parallel}(T)/H_{cb}(T)=2(\sqrt{6})\lambda_e(T)/d, \tag{2}$$

where $\lambda_e(T)$ is the penetration depth in the equilibrium state (i.e., in weak fields). This result is valid for films of thickness d satisfying the inequality

$$d<5^{1/2}\lambda_e(T), \tag{2a}$$

which is the condition for the transition to be of second order. In such a second-order transition, as H is increased toward H_T, the order parameter (energy gap, "number of superconducting electrons," or Ginzburg-Landau ψ function) approaches zero continuously, while the penetration depth λ increases from $\lambda_e(T)$ to infinity. For thicker films, the transition is of first order, with a discontinuous change of order parameter and a concomitant latent heat. These conclusions have been well substantiated experimentally, for instance, by tunnelling experiments[4] and by thermal conductivity measurements.[5]

In contrast to the results quoted above, when the field is applied perpendicular to the film surface, or when it has a component perpendicular to the surface, quite a different situation prevails. Experimentally it is known that the transition is less well defined, full normal resistance appearing only at fields about twice the field required to produce essentially normal flux penetration and thermal conductivity.[6] This can be understood in terms of a residual network of superconducting filaments left after the order parameter is reduced essentially to zero over the majority of the material. It has also been noticed that the transition in perpendicular field occurs at an $H_{T\perp}$ which is of the same order as H_{cb}, whereas $H_{T\parallel}$ may be greatly enhanced according to Eq. (2).

It is the purpose of this paper to present an elementary theory, based on the Ginzburg-Landau (G-L) theory, which describes the nature of the transition in a perpendicular field in terms of a simple model based on the concept of fluxoid quantization. The theory

* Supported in part by the National Science Foundation, the Office of Naval Research, and the Alfred P. Sloan Foundation.
[1] D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952).
[2] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).
[3] D. H. Douglass, Jr., Phys. Rev. Letters **6**, 346 (1961).
[4] D. H. Douglass, Jr., Phys. Rev. Letters **7**, 14 (1961).
[5] D. E. Morris and M. Tinkham, Phys. Rev. Letters **6**, 600 (1962).
[6] R. F. Broom and E. H. Rhoderick, Proc. Phys. Soc. (London) **79**, 586 (1961).

bears considerable resemblance to Abrikosov's theory[7] of type II superconductors in bulk form, and leads to an equivalent expression for the critical field. Thus it provides a simple model to help in understanding that rather mathematical paper. As will be indicated, the present theory accounts for the available data on films of thickness below 5000 Å, including both the absolute magnitude and the temperature dependence and angular dependence of the transition field. With the concepts developed, it is also easy to give an interpretation of the magnitude of both the periodic and nonperiodic quadratic changes of T_c with magnetic flux in the experiments of Little and Parks.[8]

II. THE MODEL

For simplicity, we first concentrate on finding the condition for the transition to occur, leaving aside the discussion of the approach to the transition. The only aspect of the approach that we require is the knowledge that it leads to a second-order transition, so that there is continuous variation of order parameter to zero at H_T. The most clear-cut experimental evidence that this is the case arises from the thermal conductivity measurements of Morris.[9] Because the thermal conductivity approaches the normal value continuously (but without "tailing" as in a broadened transition), these results show that the transition is second order in normal fields. This is true even in a 4000 Å indium film, which in parallel field had a first-order transition with the energy gap dropping discontinuously from about 90% of its field-free value to zero. The resistive transition and flux penetration measurements of Broom and Rhoderick[6] also suggest that the film goes continuously into the normal state, with the final restoration of full resistance occurring at very closely twice the field at which the difference in flux penetration from that in the normal state has dropped to an unmeasurably small value. The field for complete flux penetration agrees well with the "critical field" found in the thermal conductivity experiments. Thus, we take the critical field for flux penetration and thermal conductivity to be the value most apt to be predicted by a model which ignores the possibility of a residual filamentary network.

Given that the transition is second order, we can then consider the situation right at the transition, where the order parameter is vanishingly small and hence the penetration depth approaches infinity. In that case, the field penetration is complete, and the field everywhere is the applied field H. In this case, the curl of the supercurrent $\mathbf{J}_s$ is determined by the London equation (which is valid here, since $\lambda \to \infty$ and nonlocal effects are unimportant)

$$-\mathbf{H}=c\,\mathrm{curl}(\Lambda \mathbf{J}_s), \tag{3}$$

where H is simply the applied field. The parameter Λ is as usual given by

$$\Lambda=m/n_s e^2=4\pi\lambda^2/c^2, \tag{4}$$

where λ is the penetration depth. Although the actual charge carriers are $n_s/2$ pairs with charge $2e$ and mass $2m$, we note that this parameter Λ is unaffected by the change to a paired model. We must bear in mind, however, that mean-free-path limitations will increase λ, and hence Λ. We will also relate n_s to its value n_s^0 in equilibrium at $T=0$ by the order parameter $\omega=n_s/n_s^0$. The order parameter will vary between 0 and 1, depending on both temperature and applied fields. Integrating Eq. (3), we have the fluxoid Φ of any closed loop to be

$$\Phi=\int\int_S \mathbf{H}\cdot d\mathbf{S}+c\oint_s \Lambda \mathbf{J}_s\cdot d\mathbf{s}=0, \tag{5}$$

provided the material within the loop is superconducting so that Eq. (3) holds everywhere inside the loop. However, if there is even a point on the surface S where the material is normal, Eq. (3) fails to be true at that point, and Eq. (5) is no longer valid. Rather one has only the weaker result that

$$\Phi=\int\int_S \mathbf{H}\cdot d\mathbf{S}+c\oint_s \Lambda \mathbf{J}_s\cdot d\mathbf{s}=n\varphi_0, \tag{6}$$

where

$$\varphi_0=hc/2e=2.07\times10^{-7}\ \text{G-cm}^2 \tag{7}$$

is the well-known flux quantum for pairs. It is easily seen that Eq. (6) is equivalent to the Bohr-Sommerfeld quantum condition applied to pairs since

$$\int\int \mathbf{H}\cdot d\mathbf{S}=\oint_s \mathbf{A}\cdot d\mathbf{s},$$

and since

$$\Lambda J_s=\left(\frac{m}{n_s e^2}\right)(n_s e v)=\frac{(2m)v}{(2e)},$$

so that Eq. (6) is equivalent to

$$\oint_s \mathbf{p}\cdot d\mathbf{s}=\oint\left[(2m)\mathbf{v}+\frac{(2e)}{c}\mathbf{A}\right]\cdot d\mathbf{s}=nh. \tag{8}$$

Now consider a circular loop of radius r centered on a normal spot. Then using cylindrical symmetry, Eq. (6) becomes

$$J_s(r)=(n\varphi_0-\pi r^2 H)/2\pi r c\Lambda. \tag{9}$$

[7] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **32**, 1442 (1957) [translation: Soviet Phys.—JETP **5**, 1174 (1957)].
[8] W. A. Little and R. D. Parks, Phys. Rev. Letters **9**, 9 (1962).
[9] D. E. Morris, Ph.D. thesis, University of California, Berkeley, 1962 (unpublished).

The associated kinetic energy density is

$$T(r)=\tfrac{1}{2}n_s m v_s^2=\tfrac{1}{2}\Lambda J_s^2=\frac{1}{2\Lambda}\left(\frac{n\varphi_0-\pi r^2 H}{2\pi rc}\right)^2. \quad (10)$$

Introducing the order parameter

$$\omega=n_s/n_s^0=\Lambda_0/\Lambda, \quad (11)$$

this becomes

$$T(\omega,r)=\frac{\omega}{2\Lambda_0}\left(\frac{n\varphi_0-\pi r^2 H}{2\pi rc}\right)^2. \quad (12)$$

This term must be added to the usual G-L free energy difference expression,[2,10] namely,

$$f(\omega,T)=-a(T)\omega+\tfrac{1}{2}b(T)\omega^2, \quad (13)$$

where

$$a(T)=\frac{H_{cb}^2}{4\pi}\left[\frac{\lambda_e(T)}{\lambda_e(0)}\right]^2 \text{ and } b(T)=a(T)\left[\frac{\lambda_e(T)}{\lambda_e(0)}\right]^2. \quad (14)$$

Since ω will, in general, depend on r [so as to minimize (12)], we must also include the G-L term in $|\nabla\omega|^2$ which represents the energy increase associated with a spatial variation of the magnitude of the order parameter. This term is

$$T_1(\omega,r)=\frac{n_s^0\hbar^2}{8m}\left|\frac{d\psi}{dr}\right|^2=\frac{\hbar^2}{32e^2\Lambda_0}\frac{1}{\omega}\left(\frac{d\omega}{dr}\right)^2, \quad (15)$$

where $\omega=|\psi|^2$, ψ being the Ginzburg-Landau effective wave function of pairs normalized to unity at $T=0$.

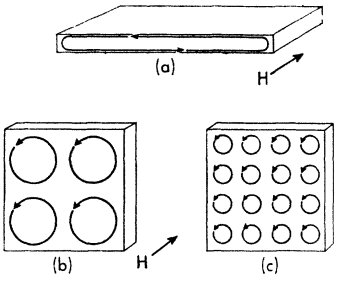
Rather than attempting a direct solution of the complete variational problem of minimizing the over-all free energy, let us first examine the problem qualitatively. From Eq. (12) we see that if $n=0$, $T\to\infty$ as ωH^2r^2. This would soon lead to values in excess of the condensation energy, Eq. (13), and the critical field would depend on specimen size and be very small for macroscopic specimens. This indicates that to maintain a superconducting state in the presence of finite fields, we must have flux penetrating through in a uniform way, with a nearly uniform density of closely packed "vortices" of current everywhere. The contrast between this vortex geometry and the usual parallel field geometry is illustrated in Fig. 1.

Now consider one such vortex containing n flux quanta. Since the field penetrates uniformly, the over-all radius R of the vortex will be such that

$$\pi R^2 H=n\varphi_0, \quad (16)$$

if we ignore errors due to the fact that circular cells will not pack to cover a surface. At the radius R, Eq. (9) tells us that J_s, and hence T, is zero. As one comes

FIG. 1. Schematic diagram of current configuration in parallel and perpendicular field cases. In parallel field geometry (a), the width of the loop is limited by film thickness. In perpendicular field geometry, size of vortex can adjust depending on field strength so as to minimize energy. Configuration (c) corresponds to higher field strength than (b), so that smaller vortices contain one flux quantum.



in toward the center, one has

$$T(\omega,r)=\frac{\omega(r)}{2\Lambda_0}n^2\varphi_0^2\frac{(1-r^2/R^2)^2}{(2\pi rc)^2}. \quad (17)$$

Even allowing for the volume element $2\pi r dr$, this gives a divergent integral unless $\omega(r)$ goes to zero at the origin. Consideration of the configurational energy T_1 given by Eq. (15) shows that it leads to the same conclusion. Application of the Euler equation obtained from applying the calculus of variations to minimization of the total free energy shows that ω should go to zero as r^{2n}, where n is the number of flux units in the vortex. This suggests using a simple trial function

$$\omega(r)=\omega_0(r/R)^\alpha, \quad (18)$$

assumed to hold all the way from $r=0$ to R. If one does this, one can compute the free energy difference per unit volume with H, n, and α as parameters. The result is

$$\Delta G=\frac{H\varphi_0\omega_0}{4\pi c^2\Lambda_0}\left[\frac{8n}{\alpha(\alpha+2)(\alpha+4)}+\frac{\alpha}{4n}\right]-a\omega_0\left(\frac{2}{\alpha+2}\right)+\frac{b}{2}\omega_0^2\left(\frac{1}{\alpha+1}\right). \quad (19)$$

In this, the first term in the bracket arises from the kinetic energy of the current circulating in the vortices, whereas the second arises from the gradient of the order parameter. As might be expected, for a given distribution of ω in the vortex, specified by the parameter α, the kinetic energy per unit area increases as n, whereas the gradient term falls as $1/n$. This behavior is qualitatively reasonable since with increase in n, fewer but larger vortices/area are required to carry the total flux. This leads to less energy from rapid variation of the order parameter, but more kinetic energy from the larger currents that must flow to maintain fluxoid quantization.

If one now examines Eq. (19), one notices that the maximum field in which $\omega_0>0$ can be sustained is de-

[10] J. Bardeen, in *Handbuch der Physik*, edited by S. Flügge, (Springer-Verlag, Berlin, 1956), Vol. 15, p. 324.

termined by setting the coefficient of the term linear in ω_0 equal to zero. This leads to the following expression for the transition field, namely,

$$H_T=\frac{4\pi c^2\Lambda_0 a}{\varphi_0}\frac{1}{[4n/\alpha(\alpha+4)+\alpha(\alpha+2)/8n]}. \quad (20)$$

The variational problem is then equivalent to finding n and α so as to maximize H_T. If one treats α and n as continuous variables, the optimum value occurs as α and n both approach zero, maintaining the relation $\alpha=2n$, in which case the bracketed quantity goes to unity.[11] To get the best physical solution, n must take its lowest nonzero integral value, namely, $n=1$. In this case the minimum value of the bracketed quantity is approximately 1.1. On the other hand, if one lets $n\to\infty$, the minimum value increases only to $\sqrt{2}$. In view of the crudity of the variational function, this increase in H_T is hardly even reliable. However, if instead of finding only H_T, one computes ΔG for $H<H_T$, one finds a clear optimum for n and α small. From these results we conclude that the optimum configuration is one in which the flux penetrates in fluxoids, each containing a single unit of flux. However, it appears that the variation with n may be weak enough so that physical inhomogeneities could shift this result to allow a coarser grained current pattern. This qualification is particularly necessary because of the extremely limited class of variation functions we have used.

Because of the very restricted trial function used to obtain Eq. (20), the results described above provide only a sort of lower limit for H_T. Moreover, the model replaces the real fluxoid "cells" by a circular approximation. Thus, even a rigorous solution to the variational problem, as set here, would not be an exact solution for the physical problem. Accordingly, in our comparison with experiment we shall simply set the bracket in Eq. (20) equal to unity, the absolute minimum determined above. If we also replace the parameter $a(T)$ by its value given in Eq. (14) and express Λ_0 in terms of the equilibrium penetration depth λ_e, Eq. (20) becomes

$$H_T(T)=\frac{4\pi\lambda_e^2(T)H_{cb}^2(T)}{\varphi_0}=6.06\times10^7\lambda_e^2(T)H_{cb}^2(T), \quad (21)$$

which is our fundamental result. Since φ_0 is a universal constant, and λ_e and H_{cb} are quite well known from other experiments, this leads to a parameter-free prediction of the critical field H_T. It is perhaps not surprising that this result is precisely equivalent to that of Abrikosov[7] for the critical field H_{c2} of bulk sample type II superconductors, in which the flux is shown to penetrate in a vortex structure similar to that described here. Explicitly, he finds $H_{c2}=\sqrt{2}\kappa H_{cb}$, where $\kappa=\sqrt{2}(e^*/\hbar c)\delta_0^2H_{cb}$. Our result is equivalent, since $e^*=2e$ and $\delta_0=\lambda_e$. Further, since $\lambda_e^2=\lambda_L^2(\xi_0/l)$ when $l\ll\xi_0$, the large value of H_{c2} for dirty superconductors is seen to follow naturally.

In order to facilitate comparison with experiment, let us approximate the temperature dependences in Eq. (21) by the usual Gorter-Casimir ones, namely $\lambda_e^2(t)=\lambda_e^2(0)(1-t^4)^{-1}$ and $H_{cb}(t)=H_{cb}(0)(1-t^2)$, where $t=T/T_c$. Then Eq. (21) becomes

$$H_T(t)=\frac{4\pi\lambda_e^2(0)H_{cb}^2(0)}{\varphi_0}\left(\frac{1-t^2}{1+t^2}\right). \quad (22)$$

Since $\lambda_e(0)$ is roughly 500 Å for typical soft superconductors with electronic mean free paths not too severely limited by film thickness, lattice imperfection, or impurity, Eq. (22) leads to the prediction that at low temperatures H_T should be proportional to the square of H_{cb}, namely,

$$H_T(0)\approx1.5\times10^{-3}H_{cb}^2.$$

This is a surprising result, considering the experimentally known fact that in magnitude $H_T\approx H_{cb}$. The reason for this apparent coincidence can only be that

$$\varphi_0\approx4\pi\lambda_e^2(0)H_{cb}(0).$$

Relations among the parameters of superconductors given by the BCS theory[12] can explain this. If one uses the usual free-electron model for the normal state parameters, one finds that

$$\varphi_0=hc/2e=(2/3)^{1/2}\pi^2\xi_0\lambda_L(0)H_{cb}(0). \quad (23)$$

Thus the requirement for the coincidence that $H_T\approx H_{cb}$ is equivalent to the requirement that

$$\lambda_e^2(0)\approx(2/3)^{1/2}(\pi/4)\xi_0\lambda_L(0).$$

But according to the BCS theory, in the limit of $\xi_0\gg\lambda_L$ with diffuse surface scattering one has

$$\lambda_\infty^3(0)=(3^{1/2}/2\pi)\xi_0\lambda_L^2. \quad (24)$$

Since the two numerical coefficients are similar, these two expressions for $\lambda^2(0)$ differ only by a factor of roughly $(\xi_0/\lambda_L)^{1/3}$, which is typically about 2 and depends relatively weakly on the material at hand. Thus there is a clear explanation of the approximate numerical coincidence of H_T and H_{cb} in typical cases.

[11] The fact that the most favorable value in Eq. (20) arises when $n=0$ and $\alpha=0$, corresponding to $\omega=\omega_0$ everywhere, might appear to contradict our original qualitative observation that $n=0$ could not be the lowest state for a macroscopic sample in a finite field. More careful consideration, however, shows that when $n=0$, the order parameter has a spatial variation approximating $\omega_0\exp[-(r/r_0)^2]$, where $\pi r_0^2H=\varphi_0$. Such an island of superconducting material shrinks in radius as H increases, ending up with a radius only $\approx\xi_0$ at the final transition field, which is the same as found below for $n>0$. However, a macroscopic system would nucleate fluxoid vortices long before that point because of the more favorable free energy for the whole of any film whose surface dimensions exceeded ξ_0.

[12] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

Finally, before passing on to a detailed comparison with experimental results, let us consider the angular dependence of the critical field according to our model. From the free-energy expression, Eq. (19), we see that a perpendicular field component produces a contribution *linear* in the applied field to be balanced against the condensation energy. By contrast, a field component in the plane of the film produces a quadratic effect. The reason for this difference is evident from Fig. 1. In the parallel orientation the important dimension of the current loops is fixed by the film thickness, hence is constant, and the energy increases as H^2; on the other hand, in the perpendicular orientation, the size of the current loops scale down as H increases, leaving only a residual linear dependence. From this argument, we see that for thin films we expect a critical field vs angle relation of the form

$$H_T \sin\theta/H_{T\perp}+(H_T\cos\theta/H_{T\parallel})^2=1, \qquad (25)$$

where $H_{T\parallel}$ is given by Eq. (2), $H_{T\perp}$ by Eq. (21), and where θ is the magnitude of the angle of the field from the plane of the film. For a thin film, $H_{T\perp}\ll H_{T\parallel}$, and the first term will dominate over a considerable angular range. The fact that the variation is with $\sin\theta$ rather than $\sin^2\theta$ is important for explaining the extreme sensitivity of critical field measurements to small perpendicular field components. If the film thickness $d>5^{1/2}\lambda_e(T)$, the transition in parallel field becomes first order, and the simple formula Eq. (25) will no longer be reliable.

III. COMPARISON WITH EXPERIMENT

The two most extensive sets of experimental data available for comparison with the theory are the thermal conductivity measurements of Morris[5,9] and the resistive transition data of Rhoderick.[13] Morris determined the critical field, as indicated by attainment of the thermal conductivity of the normal state, for films of tin, indium, and lead, at various temperatures, and in the case of lead at a range of intermediate angles between normal and parallel fields. Rhoderick measured the resistive transitions of tin films of various thicknesses over a wide range of temperatures. The interpretation of Rhoderick's data is furthered by the flux penetration measurements of Broom and Rhoderick.[6] The latter showed that flux penetration appeared to be complete at very nearly half the field at which full normal resistance was restored. Since this full flux penetration value agrees well with the field for normal thermal conductivity, we take this value to represent the establishment of the normal state except for filaments which keep the electrical resistance below its normal value. Since the extensive data of Rhoderick give only the resistive transitions, to allow comparison with Morris' data on a comparable basis, we eventually divide all the resistive critical fields by a factor of two.

[13] E. H. Rhoderick, Proc. Roy. Soc. (London) **A267**, 231 (1962).

TABLE I. Perpendicular critical field data of Morris, based on thermal conductivity, and penetration depth deduced from them using Eq. (22). The extrapolation to $H_{T\perp}(0)$ from $H_{T\perp}(t)$ is made using a factor of $(1+t^2)/(1-t^2)$.

Film	Thickness (Å)	t	$H_{T\perp}(t)$ (exp) (Oe)	$H_{T\perp}(0)$ (extrap) (Oe)	$H_{cb}(0)$ (Oe)	$\lambda_e(0)$ (Å)
In IV	4000	0.36	110	143	269	570
		0.66	66	169	269	620
Sn II	2600	0.32	150	184	305	570
Pb II	500	0.30	1110	1330	805	580
		0.64	525	1260	805	565

We start by comparing Morris' data for H_T with the values given by Eq. (22). Since an *a priori* estimate of $\lambda_e(0)$ will be made somewhat uncertain by mean-free-path effects, it is perhaps most illuminating to use Eq. (22) and the observed $H_{T\perp}$ to compute $\lambda_e(0)$ to see if the values found are reasonable and consistent. This is done in Table I. We note that the inferred penetration depths are all in quite reasonable agreement with what one would estimate allowing for mean-free-path effects. The temperature-dependence data are meager, but what there are show good agreement for the thin lead film, but poorer agreement for the thick indium film. Finally, we note that if one considers the data at low reduced temperatures, one finds the predicted proportionality between H_T and the square of H_{cb}, rather than H_{cb} itself.

Next let us compare Eq. (22) with the extensive data of Rhoderick.[13] We take data for H_T vs t^2 for various thickness tin films from his Fig. 6. To allow a more critical examination of the temperature dependences, in our Fig. 2 we have replotted his data for several representative films with the observed H_T in each case

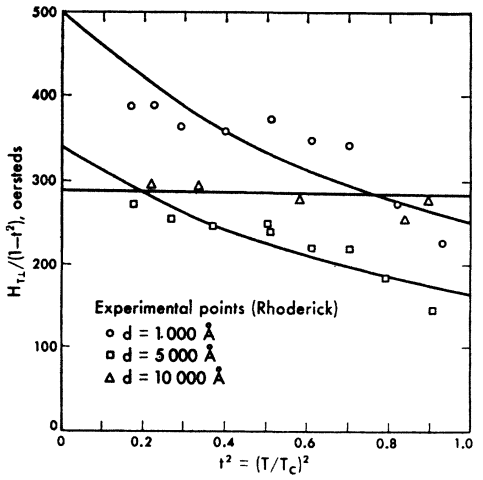


FIG. 2. Temperature dependence of critical field for restoration of complete normal resistance. Data are from Rhoderick, reference 13. To allow critical examination of the data, $H_T/(1-t^2)$ is plotted vs t^2, where $t=T/T_c$. If $H_T\sim H_{cb}$, the data fit the horizontal line. If H_T follows Eq. (22) of the text, the data fall on the sloping curve.

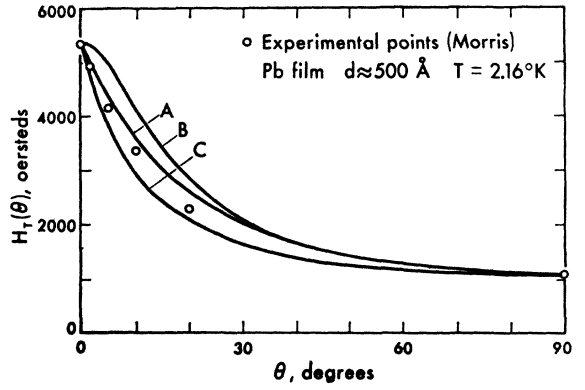


FIG. 3. Angular dependence of transition field as determined by thermal conductivity experiments of Morris, reference 9. Curves *A*, B, and *C* represent three possible interpolation functions between $H_{T\perp}$ and $H_{T\parallel}$. Curve *A* is based on Eq. (25) of this paper. Curve *C* was suggested by Morris. Curve *B* would result if the magnetic energy increased as H^2 for both perpendicular and parallel components.

divided by $(1-t^2)$ to take out (approximately, at least) the temperature dependence of H_{cb}. If H_T were proportional to $H_{cb}\sim(1-t^2)$, the points would fall on a horizontal line. If H_T is proportional to $(1-t^2)/(1+t^2)$, as predicted by the present model, the points should fall on a curve which drops by a factor of 2 in going from $t=0$ to $t=1$. Inspection of Fig. 2 shows that H_T for the 10 000 Å film does follow H_{cb}, but that for the 1000 Å and 5000 Å films the sloping curve corresponding to the present model gives a somewhat better fit. Rhoderick's data for other films of 600 Å and 2000 Å thickness are not plotted to avoid cluttering the diagram. They also can be fitted at least roughly by $(1-t^2)/(1+t^2)$, but the advantage is not really clean cut because of scatter in the data. Such scatter is probably unavoidable when one is trying to read the field for attainment of "full" normal resistance, a criterion which is hard to apply with precision. Thus the comparison here probably only shows that for thin films the present model gives no worse a fit for $H_{T\perp}(t)$ than does $(1-t^2)$, whereas for a thick film $H_{T\perp}$ is observed to be proportional to $(1-t^2)$ as might perhaps be expected.

To continue the comparison of the Rhoderick data with our model, Table II shows the penetration depths $\lambda_e(0)$ inferred from the extrapolated values of $H_{T\perp}(0)$ obtained from graphs such as those in Fig. 2. The indicated errors indicate reasonable limits of error for a fit to a $(1-t^2)/(1+t^2)$ temperature dependence. The "corrected" values in column 3 are half those in column 2 to allow empirically for the observed difference between the resistive transition field and the "magnetic" one. Since the 10 000 Å film appears to follow a $(1-t^2)$ temperature dependence, it was extrapolated to zero using that dependence rather than $(1-t^2)/(1+t^2)$. The values for this film are quoted parenthetically in Table II.

Inspection of the results shown in Table II reveals that $\lambda_e(0)$ displays the monotonic variation with d expected because of coherence length effects. For the thickest films, the values seem to be approaching the accepted experimental value for bulk samples, namely, 510 Å. For the thinnest film, if one takes[14] $\xi^{-1}=\xi_0^{-1}+d^{-1}$, and $\lambda=\lambda_L(\xi_0/\xi)^{1/2}$, with $\lambda_L=350$ Å and $\xi_0=2500$ Å (as quoted by BCS[12]), one obtains $\xi=485$ Å and $\lambda=790$ Å. The latter value is in quite good agreement with the 765 Å shown in the table. The over-all agreement is highly satisfactory in view of the simplicity of the analysis. This establishes the fact that Eq. (22) gives a satisfactory account of the magnitude of $H_{T\perp}$ for a wide variety of cases.

Let us now test Eq. (25), which predicts, in particular, a dependence on the first power of the perpendicular component of the applied field. The only directly relevant data on this question seem to be those of Morris on a 500 Å lead film. His data are particularly useful since residual filaments would not obscure thermal conductivity measurements of H_T. The values of H_T which he observed at $T=2.16$°K as a function of the angle θ between the field and the plane of the film are plotted in Fig. 3, together with calculated interpolated values between the measured values at $\theta=0°$ and 90°. He also took data at $T=4.5$°K at $\theta=0$, 30°, and 90°, not plotted here. The calculated interpolation (*A*) is based on Eq. (25) of this paper. Interpolation (*B*) is based on a similar formula, but with both parallel and perpendicular components coming in quadratically as would be expected for the usual case of a susceptibility which is field independent to first order. Interpolation (*C*) is based on a similar formula in which both field components enter linearly. The latter form has no clear *a priori* justification, but it was proposed by Morris[9] as giving a reasonably good fit to his data. Although agreement is not perfect, the interpolation (*A*) based on Eq. (25) seems to give a better account of the data than either (*B*) or (*C*). Specifically, (*B*) falls much too slowly for small values of θ because it involves $\sin^2\theta$. Since (*C*) also uses a

TABLE II. Thickness dependence of critical fields. The data are from Rhoderick (reference 13) extrapolated to $T=0$ as indicated in Fig. 2. The numbers in the third column are half those in the second to give estimate of critical field for "magnetic" transition from the measured resistive transition (see text). Final column is calculated using Eq. (22).

d (Å)	$H_{T\perp}(0)$ (Oe)	$H_{T\perp}(0)$ (corrected) (Oe)	$\lambda_e(0)$ (Å)
600	660±60	330	765
1000	500±50	250	665
2000	370±40	185	575
5000	340±30	170	550
10 000	(290±20)	(145)	(510)

[14] M. Tinkham, Phys. Rev. **110**, 26 (1958); P. B. Miller, *ibid.* **113**, 1209 (1959).

linear dependence on $\sin\theta$, it is about equally good as (A) for small angles. However, for large angles (A) gives a better fit, especially at the higher temperature (not plotted) where the single experimental point at an intermediate angle (30°) falls above all three interpolated curves, and hence considerably closer to (A) than to (C). Thus, on an over-all basis (A) is preferable on the basis of goodness of fit as well as *a priori* justification.

Summing up the results of this section, we have found that the predictions of our model appear to be in good agreement with the observed critical fields of thin ($d<\xi_0$) films of tin, lead, and indium. It predicts the angular dependence, the temperature dependence, the slight thickness dependence, and the absolute magnitude of H_T as determined from thermal conductivity or flux penetration experiments, which are not obscured by filamentary effects. Complete normal resistance is only restored at about twice the "magnetic" or "thermal conductivity" critical field predicted by the model.

IV. DISCUSSION

In the previous section, we have seen that the proposed model gives a satisfactory account of the observed critical fields. In fact, it is in principle limited to that purpose by the simplifying assumption that the order parameter ω is sufficiently small that penetration is complete and H is uniform in space. None the less, it would be desirable to have at least a qualitative picture of how the superconductor reacts to a normally incident field all the way from zero field up to the transition region. Since in this case H is no longer uniform and equal to the applied field, we must supplement the free energy density expression used previously by adding the customary term $H^2/8\pi$. This term evidently favors keeping the field as uniform as possible.

Now we consider a simple idealized model in which each flux quantum goes through the film as a uniform field over a circular region of radius R_1, over which the order parameter increases linearly with r to a value ω_0 which obtains outside the regions of flux penetration. (The linear dependence is near the variational optimum although not correct near $r=0$. This model is admittedly not entirely self-consistent, since the falloff of H to zero would be rounded instead of square, but it is qualitatively correct.) For this model, the kinetic energy and $|\nabla\omega|^2$ terms give contributions independent of R_1 but the condensation energy naturally favors $R_1\to 0$, so that $\omega=\omega_0$. This condensation energy term is countered, however, by the field energy, $H^2/8\pi$, which favors $R_1=R_0$, the radius corresponding to uniform flux penetration. Minimizing the total free energy, we find

$$\pi R_1^2=\frac{\varphi_0}{H_{cb}(T)}\frac{\lambda(0)}{\lambda(T)}\left(\frac{3\pi}{2\omega_0}\right)^{1/2}. \tag{26}$$

If we further assume that $\omega_0=\omega_e(T)$, then this reduces to

$$\pi R_1^2=\frac{\varphi_0}{H_{cb}(T)}\left(\frac{3\pi}{2}\right)^{1/2}, \tag{27}$$

which shows that within our approximation the field inside each region of flux is of the order of the bulk critical field. Given the relation Eq. (23), based on the BCS theory, one can express Eq. (27) for $T=0$ as

$$R_1^2=\pi^{3/2}\xi_0\lambda_L\approx\lambda_e^2(0)(\xi_0/\lambda_L)^{1/3}. \tag{28}$$

Thus each flux quantum is confined to a region with radius of the order of the penetration depth. As H is increased, more fluxoid vortices must be created, each having this same radius. Eventually, these vortices will start to fill an appreciable portion of the material. [According to Eq. (27), they would fill it all when $H=(2/3\pi)^{1/2}H_{cb}(t)\approx H_{T1}$.] When this happens, the field has become essentially uniform, and the original model becomes valid for the description of how ω_0 is then depressed from $\omega_e(T)$ down to zero at H_T.

From the above picture of the sequence of events, we see that until near H_T, the order parameter ω has a range of values from 0 to $\omega_e(T)$. All that changes with H is the fraction of the volume which is still at ω_e. This decreases linearly with H, as more vortices form. One might think this result to be at variance with the experimentally known fact[9] that the thermal conductivity increases quadratically with $H_\perp$ as well as with $H_{||}$. This is not necessarily the case, however, since the scattering of excitations by the *variation* of ω with position will largely counteract the fact that $\langle\omega\rangle_{av}$ is decreased by the presence of vortices, until the vortices "touch." Then the subsequent decrease of ω_0 and the corresponding spatially uniform approach to the normal state will cause a strong increase in thermal conductivity. The resulting dependence might well look nearly quadratic in H. Further tests of this hypothesis would be desirable.

One final remark is that the inhomogeneities present in real samples of even soft superconductor films will be expected to modify these results considerably. They will produce barriers which impede the free motion of the flux quanta in from the edges, which is envisioned in the model. They will certainly produce local variation in the ease of flux penetration, leading to spatial inhomogeneities on a scale large compared to that of a single quantum. Broom and Rhoderick[6] already have concluded that that is the most likely interpretation of the structure they observed in the field penetration, since the characteristic period of the variation was equal to the resolution limit of their apparatus. Another evidence of complication is their observation of a certain amount of flux trapping after the field is removed. Evidence of the severity of these effects is also given by the photographs of domain structure in tin and lead films

obtained by DeSorbo, Newhouse, and Healy.[15] These irreversible effects have to do with the presence of physically localized structure in the film which is broken through in an irreversible discontinuous way. With hard superconductors or severely strained films, even more serious departures from our simple model are to be expected. However, one might expect the criterion for the critical field to retain considerable validity even if the low-field behavior is complicated by inhomogeneity effects.

V. VARIATION OF THE CRITICAL TEMPERATURE BY MAGNETIC FIELDS

As a final application of our theory we treat the case of the change of T_c for a superconducting cylindrical film placed in an axial magnetic field, as in the recent experiments of Little and Parks.[8] Because these experiments are carried on right at T_c, $\omega_e(T)$ is very small, so the complete field penetration model should be rigorous. Also, because the film thickness is small compared to the radius of the cylinder, the optimum configuration will have $\omega=$ const over the film to eliminate the $|\nabla\omega|^2$ term.

To get at the part of ΔT_c which is periodic in H we can treat the film as being so thin compared to the radius R that in the kinetic energy expression Eq. (12) we can set $r=R$. Then we have for the total free energy difference

$$\Delta G=-a(T)\omega+\frac{b(T)}{2}\omega^2+\frac{\omega}{8\pi^2\Lambda_0 c^2R^2}(n\varphi_0-\pi R^2H)^2. \quad (29)$$

Minimizing this with respect to ω, and then setting $\omega=0$ to find the transition condition, we obtain

$$(n\varphi_0-\pi R^2H)^2=a(T)8\pi^2\Lambda_0c^2R^2 =8\pi^2R^2\lambda_e^2(T)H_{cb}^2(T). \quad (30)$$

If we use the standard temperature dependences for $\lambda_e(T)$ and $H_{cb}(T)$, this becomes

$$(n\varphi_0-\pi R^2H)^2=8\pi^2R^2\lambda_e^2(0)H_{cb}^2(0)(1-t^2)/(1+t^2). \quad (31)$$

Expanding to first order in $\Delta t=\Delta T/T_c=1-T/T_c$, we have for the displacement in T_c

$$\frac{\Delta T_c}{T_c}=\frac{(n\varphi_0-\pi R^2H)^2}{8\pi^2R^2\lambda_e^2(0)H_{cb}^2(0)}. \quad (32)$$

We note immediately that this has a parabolic variation about the values of H which place precisely an integral number of flux quanta through the tube. The maximum drop in T_c occurs when H is exactly between two quantized values. At that point,

$$(n\varphi_0-\pi R^2H)_{\max}=\varphi_0/2. \quad (33)$$

Therefore

$$\frac{(\Delta T_c)_{\max}}{T_c}=\frac{\varphi_0^2}{32\pi^2R^2\lambda_e^2(0)H_{cb}^2(0)}. \quad (34)$$

In the experiment reported by Little and Parks,[8] $R=7\times10^{-5}$ cm. Putting in the standard values for T_c and H_{cb} for tin, we find

$$(\Delta T_c)_{\max}=[1.05\times10^{-6}/\lambda_e(0)]^2.$$

Since their estimate of $(\Delta T_c)_{\max}$ from their data is 5×10^{-4}°K, this leads to the conclusion that $\lambda_e(0)=4700$ Å, which is almost an order of magnitude larger than the usual values obtained earlier in this paper. However, since the film is only 375 Å thick and is deposited on a subtrate of glue, one would expect the effective mean free path to be very small. Based on the normal resistance,[16] one would estimate $l\leqq100$ Å. If this were the case, $\lambda\approx\lambda_L(\xi_0/\xi)^{1/2}\geqq1800$ Å, which brings the results into much better agreement. Actually one would expect that the effective mean free path might be even much less than 100 Å under the conditions of the experiment, since due to inhomogeneity one is dealing with isolated threads of superconducting material, girdling the flux, but imbedded in normal material right on the edge of transition. The diameter of these threads would be the appropriate limiting dimension, if it were less than l. Actually, of course, when the superconductivity is confined to regions small compared to ξ_0, the situation is inevitably complicated, and the residual disagreement between the expected 1800 Å and the fitted 4700 Å penetration depth may well be within the uncertainty in the relation between what is actually measured and our model of a uniform change in T_c over the entire sample, assumed homogeneous.

In this connection it should be noted that Little and Parks quote a formula based on the BCS theory which predicts that the periodic part of ΔT_c be given by

$$k\Delta T_c=\frac{\hbar^2}{16mR^2}\left(\frac{\pi R^2H-n\varphi_0}{\varphi_0}\right)^2. \quad (35)$$

This differs from our Eq. (32) by a factor of the order of $(T_c/T_F)(\xi_0/l)$, where T_F is the Fermi temperature of the electron gas. For the case at hand with $l\approx100$ Å, the formula of Little and Parks predicts an effect of about 1% that predicted by the present theory. The experimental result lies in between, somewhat closer to the prediction of the present theory. The discrepancy between these two approaches appears to have arisen from an error in the approximations used by Little. As corrected, Little's result agrees substantially with ours, as should be the case since the BCS theory should reduce to the Ginzburg-Landau theory very near to T_c.

[15] W. DeSorbo and V. L. Newhouse, J. Appl. Phys. 33, 1004 (1962); W. DeSorbo and W. A. Healy, G. E. Research Laboratory Report 61-RL-2743M, 1961 (unpublished).

[16] R. D. Parks (private communication).

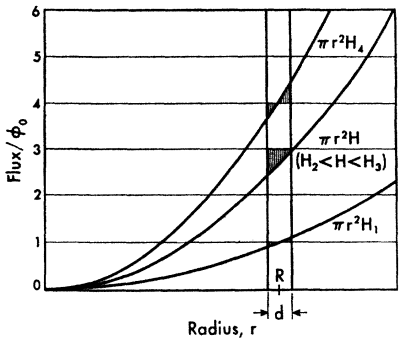


FIG. 4. Diagram indicating origin of periodic and aperiodic parabolic depression of T_c in parallel field. When $H=H_n$, the flux inside cylinder of radius R is $n\varphi_0$. There is then no circulating current at $r=R$, but to maintain fluxoid quantization, opposite currents flow for $r<R$ and $r>R$, as indicated by shading. Kinetic energy of these currents increases as H_n^2, leading to an aperiodic depression of T_c even at quantized flux values. When $H\neq H_n$, this energy is still greater, reaching a maximum when H is midway between two successive H_n. The middle curve illustrates a case where the fluxoid is $3\varphi_0$, with circulating current at all radii in the film. Evidently the kinetic energy here is much higher than when $H=H_2$ or H_3. This excess produces the periodic part of ΔT_c.

Little and Parks also observed a change in T_c which increased as H^2 in a nonperiodic manner. From inspection of Fig. 4, it is easy to see that a small effect of this sort should exist for any finite ratio of d/R. This is true because only at the radius R at which $\pi R^2H=n\varphi_0$ will there be no current density. For a finite film thickness, there will then be currents flowing one way for $r<R$ and the other way for $r>R$. From Eq. (12) or (17) we see that near R the kinetic energy density will be given approximately by

$$(\omega H^2/2\Lambda_0c^2)(r-R)^2.$$

Averaging over the film thickness, $(r-R)^2$ has a minimum value of $d^2/12$, obtained when R occurs at the middle of the thickness of the film. Thus, a term

$$\omega H^2d^2/24\Lambda_0c^2,$$

should be added to the periodic term treated above in Eq. (29). Comparing the two terms, it is evident that the ratio of the pure quadratic term to the periodic term is

$$\frac{1}{3}\frac{d^2}{R^2}\left(\frac{H}{H-H_n}\right)^2, \tag{36}$$

where $H_n=n\varphi_0/\pi R^2$ is the field giving the nth minimum in the periodic variation. Thus, the pure quadratic term has a coefficient which is only $(d^2/3R^2)$ that of the periodic term in $(H-H_n)^2$. For the film used in the Little-Parks experiment, $(d^2/3R^2)\approx 10^{-3}$, whereas they found a pure quadratic term down by only about 10^{-1}. Since Λ has cancelled out in the ratio, the theoretical ratio depends only on geometrical factors. Hence it should be more reliable than the absolute value of the periodic effect, computed above, and the discrepancy is harder to explain.

One way to account for the large observed quadratic background is to assume that the field is not exactly axial to the cylindrical shell. In that case there will be a field component perpendicular to the axis. This component will induce supercurrent circulation along the length of the cylinder, halfway around one end, then back on the other side, closing on itself. Applying Eq. (5) to such a path, one finds

$$J_s\approx H_\perp R/c\Lambda,$$

and hence a kinetic energy density

$$\tfrac{1}{2}\Lambda J_s^2\approx(\omega H_\perp^2/2\Lambda_0c^2)R^2. \tag{37}$$

This term is $(12R^2/d^2)(H_\perp/H_{||})^2$ times the effect of the parallel field due to finite wall thickness. To account for the observed magnitude, this ratio must be ~ 100. For the given values of R and d, this requires that $(H_\perp/H_{||})^2$ be about 0.025, corresponding to a 9° misalignment of the field. A physical misalignment of this magnitude is unlikely, but it is possible that field distortions due to screening currents arising in the ac experimental technique used might account for an effect of this magnitude. Also, because of the very different path of the circulating current, sample inhomogeneities in T_c would be expected to produce a different sensitivity for this geometry than for the purely longitudinal field case.

One might wonder why the characteristic first-order field effects from flux quanta threading the sample, as discussed earlier in this paper, are not observed from the assumed perpendicular field components. The explanation lies in the small radius of the tube, namely 0.7 μ. This is less than the radius of a *circular* fluxoid vortex for the small normal component of field we are dealing with. This forces the current into a rectangular loop of length L such that $L\approx\varphi_0/2RH_\perp$. As long as $L\gg R$, the value of L drops out of the size of the energetic effect, and the energy $\sim H^2$, as observed. The situation is essentially that shown in Fig. 1(a). For somewhat larger perpendicular fields, however, the present viewpoint does suggest that a breakup of the tube into vortices, with effects linear in H, might be observable.

The various results of this section may be summarized by collecting Eq. (32) together with results equivalent to Eq. (36) and (37) into a single expression for the depression of the critical temperature due to a field H at an angle θ to the axis of a cylindrical superconducting shell of radius R and thickness $d\ll R$. This result is

$$\frac{\Delta T_c}{T_c}=-\frac{1}{8}\frac{R^2}{\lambda_e^2(0)H_{cb}^2(0)}\times\left[(H\cos\theta-H_n)^2+\frac{1}{3}\frac{d^2}{R^2}H^2\cos^2\theta+4H^2\sin^2\theta\right], \tag{36}$$

where H_n is the field which would produce precisely n

flux quanta within a circle halfway through the thickness of the wall of the cylinder, if applied directly along the axis of the cylinder.

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Threshold for Electron Radiation Damage in ZnSe*

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A threshold for the displacement of an atom from the ZnSe lattice by electron bombardment has been observed at 240 keV. An electron of 240 keV transfers a maximum energy of 8.2 eV to the selenium atom and 10 eV to the zinc atom. The displacement is observed by the production at 85°K of a broad fluorescence band which is resolvable into two overlapping bands with peaks at 5460 and 5850 Å. The radiation damage anneals completely at a temperature of 160°K.

INTRODUCTION

LIKE CdS and ZnS, ZnSe is a II–VI compound semiconductor often grown by vapor-phase deposition at high temperature under various conditions of atmospheric control.[1–3] This method of growth results in crystals of questionable stoichiometry and quality. Many of the fluorescence properties of these compounds are believed to be a result of crystal defects in conjunction with or independent of chemical impurities.

Electron bombardment has proven to be a useful tool to produce defects in silicon which involve vacancy-impurity[4,5] as well as multiple-vacancy complexes.[6] Earlier studies in this laboratory have shown that it is possible to isolate defects of different atoms in compound semiconductors by measuring the threshold energies for the production of various fluorescence bands in these materials.[7,8] This latter technique has been applied to single-crystal ZnSe and the results of bombardment experiments with electrons in the energy range 225 to 500 keV are described here.

EXPERIMENTAL

The crystals used in these experiments were grown by vapor phase deposition by L. C. Greene of this laboratory. The electron bombardments were carried out in vacuum with a Van de Graaf accelerator at a dc level of irradiation of 4 to 20 μA/cm^2, at a temperature near liquid nitrogen temperature. The fluorescence was measured with a Perkin-Elmer glass prism spectrometer with a type 6199 photomultiplier detector. The infrared fluorescence was measured with a lead sulfide detector. The spectrum following 500 keV bombardment was taken with a Cenco 1-m grating spectrometer with 103A-F film. During bombardment the crystals were mounted on a cold finger beneath a liquid nitrogen Dewar in the beam of the accelerator. The fluorescence was observed through a quartz window. The fluorescence was excited by electrons with an energy of 275 keV at an intensity of 4 μA/cm^2. The energy was so chosen that the intensity did not change appreciably in the five minutes required to scan the wavelength region of interest.

DATA AND RESULTS

A. Electron Bombardment

Figure 1 shows the fluorescence spectrum of a single crystal of ZnSe before and after bombardment by 10^{16} electrons/cm^2 at an energy of 500 keV at 85°K. The fluorescence following bombardment has been resolved into two bands with a symmetrical intensity distribution and peaks at 5460 and 5850 Å. The wavelengths

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[1] R. Frerichs, Phys. Rev. **72**, 594 (1947).
[2] D. C. Reynolds and S. J. Czyzak, Phys. Rev. **79**, 543 (1950).
[3] F. A. Kroger, H. J. Vink, and J. Van den Boomgaard, Z. Physik. Chem. (Leipzig) **203**, 1 (1954).
[4] G. D. Watkins and J. W. Corbett, Phys. Rev. **121**, 1001 (1961).
[5] J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, Phys. Rev. **121**, 1015 (1961).
[6] J. W. Corbett and G. D. Watkins, Phys. Rev. Letters **7**, 314 (1961).
[7] B. A. Kulp and R. H. Kelley, J. Appl. Phys. **31**, 1957 (1960).
[8] B. A. Kulp, Phys. Rev. **125**, 1865 (1962).