Gor'kov-Goodman relation in low-κ aluminum films*

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From measurements of the critical field H_{c2} in thin films of superconducting aluminum we have been able to verify the Gor'kov-Goodman relation between the Ginzburg-Landau parameter and normal-state resistivity ρ_N. The proportionality is close to that predicted from the specific heat, however, the intercept at $\rho_N = 0$ agrees with nonlocal theory rather than Gor'kov's local calculation. Our work differs from other thin-film measurements in that we use tunneling to determine the transition at H_{c2} and because we extrapolate against normal-state resistivity rather than film thickness. The temperature dependence of H_{c2} is found to agree with the calculations of Maki.

INTRODUCTION

Within the framework of the Ginzburg-Landau (GL) theory[1] one can calculate the critical field H_{c2} for nucleation of bulk superconducting regions. The GL theory in this form is valid near T_c, the transition temperature, and in the limit of local electrodynamics, i.e., $\lambda(T) \gg \xi_0$. Here $\lambda(T)$ is the temperature-dependent penetration depth and ξ_0 is the coherence length. These two conditions are fulfilled near H_{c2} provided that the order parameter goes continuously to zero at H_{c2}, i.e., there is a second-order phase transition. In this case the GL equation can be linearized to obtain the well-known result[2]

$$H_{c2}(T) = \kappa\sqrt{2}\,H_c(T) \ . \tag{1}$$

Here κ is the GL parameter and $H_c(T)$ is the thermodynamic critical field. There is an additional complication stemming from surface superconductivity. In a parallel field superconductivity can be nucleated at a field $H_{c3} > H_{c2}$ which can be calculated exactly like Eq. (1) except for the boundary condition. St. James and de Gennes[3] show that

$$H_{c3} = 1.695\kappa\sqrt{2}\,H_c \ , \tag{2}$$

whereas for fields perpendicular to the surface, such as thin-film transitions in a perpendicular field, Eq. (1) is valid. We use Eq. (1) to determine κ from our experimental measurements of the perpendicular critical field in thin films, with the final goal the verification of the Gor'kov-Goodman relation[4,5]

$$\kappa = \kappa_0 + 7500\gamma^{1/2}\rho_N \ , \tag{3}$$

where κ_0 is the value of κ for a pure, bulk superconductor, γ is the coefficient of the linear term in the temperature-dependent specific heat, and ρ_N is the normal-state resistivity. Before discussing the experiments and results, we make some general comments on measurements of κ.

For extreme type-II superconductors, i.e., $\kappa \gg 1$, the transition at H_{c2} is known to be second order, so Eqs. (1) and (2) are valid and are a reliable method of determining κ. There are two other cases of interest when the linearized GL theory has been used to determine κ. These are supercooling[6-10] and thin-film transitions.[11,12] We first consider the transition of a thin film which is a type-II superconductor in the bulk. This film will have a second-order transition and the critical field is either H_{c2}, H_{c3}, or an intermediate value, depending on the orientation of the field. On the other hand, films of bulk type-I superconductors have second-order transitions only if they are sufficiently thin. In a parallel field, Douglass[13] has measured the energy gap by tunneling and has shown that the transition is first order for thick films ($d > \frac{1}{2}\sqrt{5}\lambda$) and second order for thin films, in accordance with theoretical predictions.[14] In a perpendicular field, the author[15] has used tunneling to show a first-order transition for thick films (with supercooling effects), while below a critical thickness[11,15,16] the films are reversible, indicating a second-order transition. These thinner films are essentially type II with single quantum vortices, even though they have $\kappa < 1/\sqrt{2}$. This behavior was predicted by Tinkham,[17] and experimentally verified by others.[15,16] Note that these thin films are reversible, so that H_{c2} is the actual critical field even though it can be considerably less than the thermodynamic critical field H_c (see Fetter and Hohenberg[18] for a discussion). Since the transition is of second order for sufficiently thin films, we expect Eqs. (1) and (2) to be valid and hence we can derive κ from measurements of H_{c2} or H_{c3} and H_c. In contrast, supercooling transitions are first order, as in the case of thick type-I films, so that Eqs. (1) and (2) should not be valid. In spite of this, numerous attempts[8-10] to derive κ using supercooling critical fields and Eqs. (1) and (2) have been made, with considerable discrepancy with theoretical predictions. On the theoretical side, the calculations of κ_0 by Gor'kov[4] relies on local GL theory and therefore would not be expected to be valid for an intrinsic type-I, nonlocal superconductor. Hence a comparison of κ_{sc} with GL theory[8–10] or thin-film transition data[19] seems of questionable value. The problem of nonlocality has been discussed in several places.[20,21] The main conclusion in regard to this experiment is that we can justifiably use Eq. (1) to determine κ of Eq. (3) from H_{c2} for thin films which exhibit a second-order transition. In order to check Eq. (3) against our experimental data, we must know what value of κ_0 is expected. As we mentioned above, Gor'kov's calculation was based on local electrodynamics and is therefore not applicable unless $\lambda(T) \gg \xi_0$. For pure, bulk aluminum this occurs when $1 - T/T_c \ll 10^{-3}$, which is experimentally unattainable. For this reason we should not use $\kappa_0 = 0.96\lambda_L/\xi_0$ as determined by Gor'kov, with λ_L the London penetration depth. Instead we use $\kappa_0 = \lambda/\xi$, where λ is the penetration depth corrected for nonlocal effects[2] using the expression from the BCS theory. We then find $\kappa_0 \approx (480\ \text{Å})(16\,000\ \text{Å}) = 0.3$ for the intercept of the curve κ vs ρ_N.

EXPERIMENTAL

There are two unique features of our experiments in regard to verifying Eq. (3). First, we use sufficiently thin films so that Eq. (1) is valid, making it possible to follow Eq. (3) to values of κ less than $1/\sqrt{2}$. Second, we determine the transition at H_{c2} from measurements of the conductance of a tunnel junction, rather than from the more usual techniques using magnetization, susceptibility, or resistive transitions. The tunneling technique has intrinsic advantages over these others since it probes the bulk of the film and is relatively insensitive to contributions from the edges of the films. It is also a more passive probe.

Thin films of aluminum were produced by electron-beam evaporation of 99.999%-pure aluminum onto glass substrates at about room temperature. The normal resistivity could be continuously varied by adjusting the residual oxygen pressure during evaporation. The rate of evaporation was controlled with a Sloan DTM 1000 to maintain uniformity throughout the thickness of the films. Very clean films could be produced, using a combination of the high pumping speed of a titanium sublimation pump with liquid-nitrogen-cooled fins in a 24-in. ultrahigh-vacuum system, together with evaporation rates of about 100 Å/sec. The pressure during these evaporations stayed below 3×10^{-7} Torr. In these films ρ_N was size limited due to electron scattering at the surfaces of the film. The film thicknesses ranged from 500 to 12 000 Å.

Tunnel junctions were formed by glow discharge oxidation of the aluminum followed by evaporation of a magnesium or aluminum counterelectrode. In the case of aluminum, the properties of the two

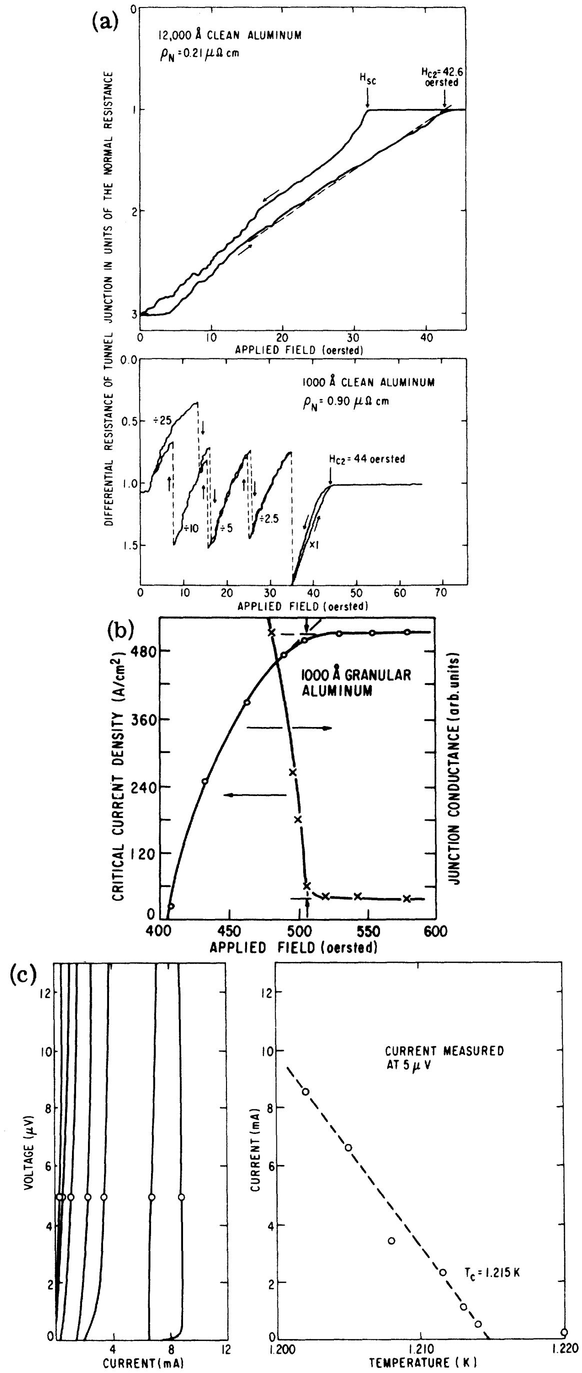

FIG. 1. (a) Critical field H_{c2} of clean aluminum films determined from the differential resistance of a tunnel junction (method A). The 1000-Å film is reversible but the 12 000-Å film shows supercooling, indicating type-I behavior. (b) Comparison of the critical field determined from the tunneling conductance (method A) and by an extrapolation of the critical current (method B). (c) Current-voltage curves at various temperatures and at constant field are shown on the left-hand side. The current at a constant voltage of 5 μV is plotted on the right-hand side to determine T_c at that applied field (method C).

films were matched as close as possible. Samples were tested in a ^{3}He cryostat in which the temperature could be conveniently varied between 0.4 and 10 K during measurements. Standard ac techniques were used to measure the tunnel junction conductance, and four terminal dc measurements on the films were used to determine their critical current. No attempt was made to cancel the earth's magnetic field, which has a component perpendicular to the films of about 0.25 G. Several procedures for determining H_{c2} were tried; all gave consistent results.

Method A. The tunneling conductance was measured at constant temperature as the field was varied from zero to above H_{c2} and back to zero. Figure 1(a) shows results on clean films of thicknesses 1000 and 12 000 Å. The thick film has hysteresis and supercooling, indicative of type-I superconducting behavior. All of the other films, which were thinner than 5000 Å, behaved like the 1000-Å film, being reversible and indicating type-II behavior. These results are consistent with the observed transition from type II to type I at about 1 μm thickness.[11]

Method B. We also measured H_{c2} from the extrapolation of the critical current density versus magnetic field. As the field increases, we find a sharp drop to roughly 50 A/cm^2 followed by enhanced superconductivity to fields significantly higher than H_{c2}. This is apparently due to edge conduction. The extrapolated value at the sharp drop agrees with the value of H_{c2} obtained from tunneling, and thus we conclude it is also a valid determination of H_{c2} [see Fig. 1(b)].

Method C. The critical current was measured versus temperature at a constant field which is applied at temperatures above T_c (in zero field). We determine $T_c(H)$ by extrapolating $I(T)$ at constant voltage and field [see Fig. 1(c)].

RESULTS AND DISCUSSION

In order to obtain κ from Eq. (1) and our measurements of H_{c2}, we need to know the thermodynamic critical field H_c. We cannot determine H_c directly, so we assume that its dependence on reduced temperature (T/T_c) is the same as pure, bulk aluminum and that $H_c(T=0)$ scales proportional to T_c, as expected for weak-coupling superconductors, based on the BCS theory. The above procedure is then equivalent to defining

$$\kappa = \frac{1}{\sqrt{2}}\left(\frac{dH_{c2}}{dT}\right)_{T_c}\left(\frac{dH_{cb}}{dT}\right)^{-1}_{T_{cb}}, \tag{4}$$

where H_{cb} and T_{cb} are taken for pure, bulk aluminum. Harris and Mapother[22] have made an accurate determination of $H_c(T/T_c)$ for pure, bulk aluminum, which gives $(dH_{cb}/dT)_{T_{cb}} = -155$ Oe/K. Table I shows the parameters for the various films measured. The results depended only on ρ_N and not the thickness as long as the critical thickness[11,15] was not exceeded, giving type-I behavior. In Fig. 2 we show the results for κ vs ρ_N (solid data points). An additional point at about 8 $\mu\Omega$ cm was determined by Ekin and Clem[23] using the same analysis. The open triangles are data points for bulk alloys of aluminum, showing that one cannot use the critical field to determine κ when it is less than $1/\sqrt{2}$. These points were determined from the critical-field measurements of Nemoz and Solecki[24] at $T/T_c = 0.8$ using the following equation [which is consistent with our determination in Eq. (4)]:

$$\kappa = \frac{1}{\sqrt{2}}\,\frac{H_{c2}(t=0.8)}{0.2T_c}\left(\frac{dH_{cb}}{dT}\right)^{-1}_{T_{cb}}. \tag{5}$$

The line through the data is the equation

TABLE I. Experimental parameters for the films used in this study, including the results of Ekin and Clem (Ref. 23).

Film thickness d (Å)	T_c (K)	$-\left(\frac{dH_{c2}}{dT}\right)_{T_c}$ (Oe/K)	κ	ρ_N ($\mu\Omega$ cm)
4500	1.215	21.7	0.10	0.17
2250	1.21	28	0.13	0.38
5000	1.196	55	0.25	0.79
1000	1.210	58	0.27	0.90
1500	1.341	290	1.32	5.0
5900[a]	1.48[a]	499[a]	2.26[a]	8.45[a]
1000	1.53	575	2.70	10.0
12 000	1.178	57	0.26[b]	0.21

[a]Average of two films which had very similar parameters from Ekin and Clem (Ref. 23).

[b]Type-I film which shows supercooling.

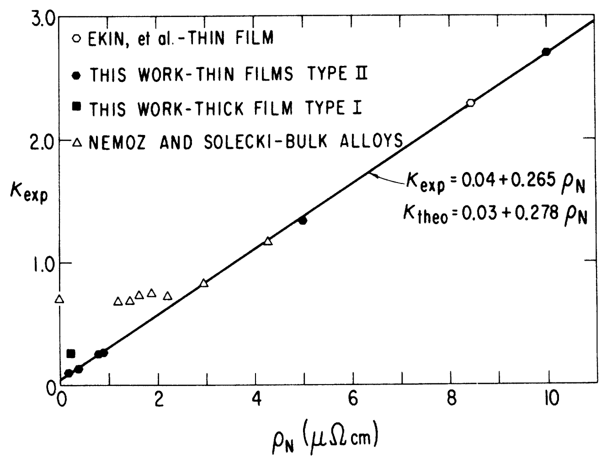

FIG. 2. Experimental values of κ plotted against ρ_N. The solid data points are from this work, with an additional point at about 8 $\mu\Omega$ cm from Ekin and Clem (Ref. 23). The open triangles are from Nemoz and Solecki (Ref. 24) for bulk alloys of aluminum. The line through the data represents the equation shown for κ_{expt}. For comparison the theoretical equation is also shown.

$$\kappa = 0.04 + 0.265\rho_N , \quad (6)$$

whose slope compares very well with the theoretical value of 0.278, using $\gamma = 1350$ erg/cm^3 K^2 and ρ_N in units of $\mu\Omega$ cm. This value of γ has been shown to be correct for granular aluminum films as well as bulk.[25] The intercept is also close to the expected value of κ_0 for pure, bulk aluminum, calculated above to be 0.03. We feel that this work adequately confirms the Gor'kov-Goodman relation in the region of $\kappa < 1/\sqrt{2}$, where it has not previously been tested. The intercept, however, is in much better agreement with the nonlocal correction to the London penetration depth than with Gor'kov's local calculation which gives $\kappa_0 = 0.96\lambda_L/\xi_0 = 0.01$.

Previous workers[11,12] have extrapolated H_{c2} measurements in thin films against thickness to determine κ_0. The objection to this procedure, particularly in the case of aluminum, is that contamination of the films during evaporation may mean that the extrapolation is not to pure, bulk aluminum, but to impure, bulk aluminum which will have a higher κ is accordance with Eq. (3). For example, Brandt *et al.*[11] determine $\kappa_0 = 0.28$, while Maloney and de la Cruz[12] find $\kappa_0 = 0.086$.

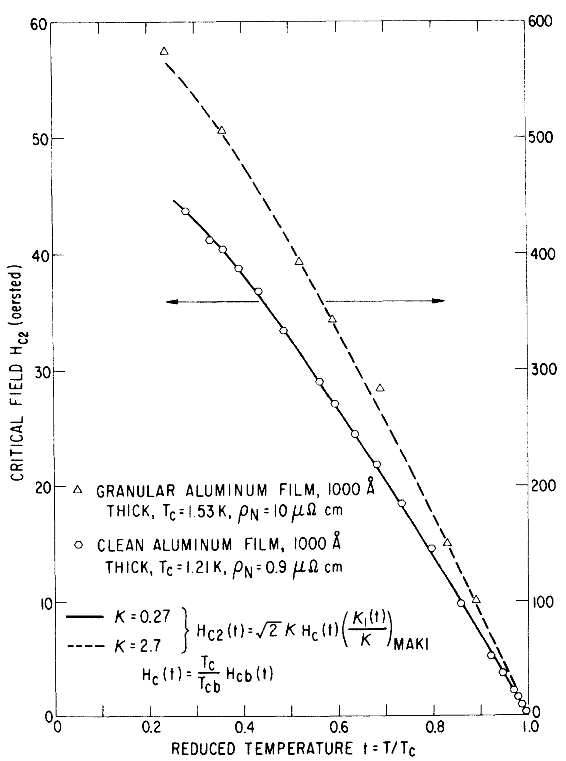

FIG. 3. Temperature dependence of H_{c2} for a clean film and a dirty film. The lines through the data are the predicted dependence based on the value of κ and the theory of Maki (Ref. 28). Note that the vertical scales differ by a factor of 10.

The critical field H_{c2} has been studied in very dirty granular aluminum films by Cohen and Abeles.[26] They report critical fields versus temperature in four samples with resisitivities at 4.2 K of 53, 153, 520, and 1000 $\mu\Omega$ cm. If we calculate κ from their data in the manner outlined above, we find values of 15, 26, 41, and 84, respectively, whereas the Gor'kov-Goodman equation using our experimentally determined slope would yield values of 14, 40, 138, and 265, respectively. There is agreement only for the lowest-resistivity sample, with the measured critical field being too small for the others. We feel that this discrepancy may be in part due to the difficulty of producing homogeneous samples, especially at very high doping levels. They measure the sample resistance versus field and find up to a 30% transition width.

The lowest value of κ we measured was 0.1, which means that the critical fields are about 14% of the thermodynamic critical field. We have an unusual situation in that a field energy density $H_{c2}^2/8\pi$, which is only 14% of the superconducting condensation energy density $H_c^2/8\pi$, can destroy superconductivity. The explanation lies in the effective penetration depth[27] for fields perpendicular to the film. Because the film is so thin there are insufficient supercurrents to effectively screen perpendicular magnetic fields, and these fields die away with an effective penetration depth λ_{eff} which can be much greater than λ. Hence the $\kappa_{eff} = \lambda_{eff}/\xi$ can be greater than $1/\sqrt{2}$, leading to a negative surface energy and single quantum vortices. The single quantum vortices have normal cores of size ξ, so the entire film is filled with normal cores at $H_{c2} \simeq \phi_0/2\pi\xi^2$, and hence this is the actual critical field. The flux quantum ϕ_0 is equal to 2×10^{-7} G cm^2. In a bulk type-I superconductor with positive surface energy one has the intermediate state with large normal regions, in which the field is H_c. Only when the applied field equals the thermodynamic critical field H_c is the entire volume filled with normal regions.

The temperature dependence of H_{c2} for two representative films, a dirty one with $\kappa > 1/\sqrt{2}$ and a clean one with $\kappa < 1/\sqrt{2}$, are shown in Fig. 3. The dependences are quite different from bulk aluminum; however, they are in excellent agreement with Maki's predictions.[28] The solid and dashed curves are obtained from

$$H_{c2}(t) = \sqrt{2}\,\kappa H_c(t)[\kappa_1(t)/\kappa] ,$$

where κ is determined above from the behavior near T_c, $H_c(t)$ is the bulk thermodynamic critical field multiplied by the ratio of the film to bulk transition temperatures, and $\kappa_1(t)/\kappa$ is determined by Maki.[28] The agreement over the entire temperature range is excellent for both films. This is not so surprising, perhaps, for the dirty film, which would be a bulk type-II superconductor, but in the clean film the type-II behavior is a result of the film being thinner than the critical thickness, which is not a part of the Maki theory. It may be fortuitous, since we should remark that the 12 000 Å type-I film was in better agreement with the Maki dependence than with bulk, although the agreement was not nearly as good.

CONCLUSIONS

In conclusion, we feel that we have adequately verified that the Gor'kov-Goodman relation[4,5] is also valid for $\kappa < 1/\sqrt{2}$, and we find good agreement with expected values of the slope and intercept. The value of the intercept κ_0 for a type-I superconductor is not given by the Gor'kov local calculation[4] but rather by using the nonlocal correction to the London penetration depth. We raise some questions about the appropriateness of comparing supercooling results[8–10] κ_{sc} with thin-film transitions[11,12] or a local calculation[4] of κ_0. Our measurements are consistent with the transition from type-I to type-II behavior in pure aluminum films at about 1 μm critical thickness.[11] Excellent agreement is found with Maki's calculation[28] of the temperature dependence of H_{c2}.

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[1]V. L. Ginzburg and L. D. Landau, Zh. Eksp. Teor. Fiz. 20, 1064 (1950).
[2]D. Saint-James, G. Sarma, and E. J. Thomas, *Type II Superconductivity* (Pergamon, Oxford, 1969), p. 43.
[3]D. Saint-James and P. G. de Gennes, Phys. Lett. 7, 306 (1963).
[4]L. P. Gor'kov, Zh. Eksp. Teor. Fiz. 36, 1918 (1959); 37, 1407 (1959) [Sov. Phys.-JETP 9, 1364 (1959); 10, 998 (1960)].
[5]B. B. Goodman, IBM J. Res. Dev. 6, 63 (1962).
[6]T. E. Faber, Proc. R. Soc. A 241, 531 (1957).
[7]J. P. Burger, in *Superconductivity*, edited by P. R. Wallace (Gordon and Breach, New York, 1964), p. 463.
[8]J. Feder and D. S. McLachlan, Phys. Rev. 177, 763 (1969).
[9]F. de la Cruz, M. D. Maloney, and M. Cardona, Physica (Utr.) 55, 749 (1971).
[10]F. W. Smith, A. Baratoff, and M. Cardona, Phys. Kondens. Mater. 12, 145 (1970).
[11]B. L. Brandt, R. D. Parks, and R. D. Chaudhari, J. Low. Temp. Phys. 4, 41 (1971).
[12]M. D. Maloney and F. de la Cruz, Solid State Commun. 9, 1647 (1971).
[13]D. H. Douglass, Phys. Rev. Lett. 7, 14 (1961).
[14]D. H. Douglass, Phys. Rev. Lett. 6, 346 (1961).
[15]K. E. Gray, J. Low Temp. Phys. 15, 335 (1974).
[16]G. J. Dolan and J. Silcox, Phys. Rev. Lett. 30, 603 (1973).
[17]M. Tinkham, Phys. Rev. 129, 2413 (1963).
[18]A. L. Fetter and P. C. Hohenberg, Phys. Rev. 159, 330 (1967).
[19]G. D. Cody, Phys. Lett. A 37, 295 (1971).
[20]J. R. Hook and J. R. Waldram, Proc. R. Soc. A 334, 171 (1973).
[21]R. A. Buhrman, Ph.D. thesis (Cornell University, 1973) (unpublished).
[22]E. P. Harris and D. E. Mapother, Phys. Rev. 165, 522 (1968).
[23]J. W. Ekin and J. R. Clem, Phys. Rev. B 12, 1753 (1975).
[24]A. Nemoz and J. C. Solecki, in *Proceedings of LT* 13, edited by K. D. Timmerhaus, W. J. O'Sullivan, and E. F. Hammel (Plenum, New York, 1974), Vol. 3, p. 95.
[25]R. L. Greene, C. N. King, R. B. Zubeck, and J. J. Hauser, Phys. Rev. B 6, 3297 (1972).
[26]R. W. Cohen and B. Abeles, Phys. Rev. 168, 444 (1968).
[27]J. Pearl, Appl. Phys. Lett. 5, 65 (1964); Ph.D. thesis (Polytechnic Institute of Brooklyn, 1965) (unpublished).
[28]K. Maki, Physics (N.Y.) 1, 21 (1964).