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Theory of the upper critical field in layered superconductors*

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The upper critical field H_{c2} in layered superconductors is calculated from a microscopic theory in which the electrons are assumed to propagate freely within the individual layers subject to scattering off impurities and to propagate via tunneling between the layers. For the magnetic field parallel to the layers, there is a temperature $T^* < T_c$ below which the normal cores of the vortices fit between the metallic layers, removing the orbital effects as a mechanism for the quenching of superconductivity in the individual layers. In this temperature regime, $H_{c2\parallel}$ is thus determined by the combined effects of Pauli paramagnetism and spin-orbit scattering, and for sufficiently strong spin-orbit scattering rates, $H_{c2\parallel}(T=0)$ can greatly exceed the Chandrasekhar-Clogston Pauli limiting field H_P. This unusual behavior is found to be most pronounced in the dirty limit for the electron propagation within the layers and when the electrons scatter many times in a given layer before tunneling to an adjacent layer. Our results are also discussed in light of the available experimental data.

I. INTRODUCTION

Recently there has been considerable interest in the properties of layered superconductors. The most unusual of these, the transition-metal dichalcogenides intercalated with organic molecules, were first investigated by Gamble *et al.*[1] and were found to be extremely anisotropic with regard to their superconducting properties. Since then, many workers have investigated the superconductivity of these materials. Initially, much of this work was directed at studying fluctuation phenomena above the superconducting transition, in the hope of finding fluctuation behavior characteristic of a two-dimensional superconductor. After considerable effort, both theoretical[2-4] and experimental,[5,6] the consensus now appears to be that for the materials investigated to date, the fluctuation behavior is, for the most part, like that expected for a three-dimensional though highly anisotropic superconductor rather than for a two-dimensional one. Two-dimensional fluctuation behavior is expected to occur at high temperatures, above a dimensional crossover temperature, but apparently the present experimental data do not extend into this regime.

The absence of prominent two-dimensional fluctuations does not imply that the superconducting properties of these materials are not strongly effected by their two-dimensional nature, however. As we have pointed out previously,[7,8] the quasi-two-dimensional nature of these materials is expected to manifest itself most dramatically *below* T_c in the fully superconducting regime. Moreover, numerical estimates indicate that presently available materials should be favorable for the observation of these effects, if suitably good crystals are available. Specifically, we have found that if the individual layers in these materials are sufficiently decoupled, the upper critical field parallel to the layers $H_{c2\parallel}$ is not limited by the usual orbital effects (i.e., vortices) and would in fact be infinite at low temperatures in the absence of other limiting effects. One obvious possible limitation on H_{c2} is the Pauli paramagnetic limit, but other more exotic possibilities have also been considered.[9] In this paper, we present a thorough discussion of our theory of the upper critical field in layered superconductors and its physical interpretation, developing in detail the results described briefly in our earlier reports.

Historically, the first attempts to calculate the upper critical field of layered superconductors were carried out by Kats[10] and by Lawrence and Doniach[11] (LD). In these papers, the anisotropic Ginzburg-Landau (GL) equations were justified and then used to calculate $H_{c2}(\theta, T)$. It was found that sufficiently near T_c, where the GL equations are valid, H_{c2} is given by

$$H_{c2}(\theta, T)=\frac{\Phi_0}{2\pi\xi^2(T)[\cos^2\theta+(m/M)\sin^2\theta]^{1/2}}\,, \quad (1)$$

where Φ_0 is the flux quantum, $\xi(T)$ is the GL coherence length in the plane of the layers, m/M is the GL anisotropic mass ratio, and θ is the angle of the applied field measured from the direction perpendicular to the plane of the layers. Kats further suggested that for fields parallel to the layers ($\theta=\frac{1}{2}\pi$), $H_{c2\parallel}$ might be limited by the Chandrasekhar-Clogston Pauli paramagnetic limiting field,[12]

$$H_P=4T_c/\pi\mu_B\,, \quad (2)$$

where μ_B is the Bohr magneton. In this paper we use the natural units $\hbar = c = k_B = 1$.

However, since the anisotropic GL theory is only valid sufficiently close to T_c such that the GL coherence length perpendicular to the layers $\xi_z(T)$ is much larger than the layer separation s, it is not expected to be even qualitatively correct at lower temperatures where $\xi_z(T)$ can become less than or comparable to the layer separation. Moreover, since the parallel critical fields in these materials are observed to exceed the Chandrasekhar-Clogston Pauli paramagnetic limit by as much as a factor of 5,[13] ultimately any proper theory of H_{c2} must include Pauli paramagnetic limiting along with the quenching effects of spin-orbit scattering. The theory developed in this paper is free of both of these deficiencies. In addition, as indicated above, it clarifies the manner in which the two-dimensional nature of layered compounds is expected to affect their superconductivity and predicts some novel behavior in the temperature dependence of H_{c2} for layered compounds.

This more complete theory is developed in two steps. First, in Sec. II we calculate H_{c2} using the Lawrence-Doniach equation, in which layered compounds are modeled as a stacked array of two-dimensional superconductors coupled through Josephson tunneling. We find that the LD equations predict the existence of a temperature T^* less than T_c [defined by the relation $\xi_z(T^*) = s/\sqrt{2}$] below which the upper critical field parallel to the layers is infinite. We interpret this result physically as evidence that the normal cores of the vortices present in the mixed state of layered superconductors can, under the appropriate conditions, effectively fit in between the layers, thereby removing the orbital effects as a mechanism for the quenching of superconductivity. In this situation, the upper critical field parallel to the layers becomes determined by those mechanisms responsible for the destruction of superconductivity in the individual layers, and as regards $H_{c2\parallel}$, the layered compound is effectively behaving two dimensionally. Moreover, it is only for $T < T^*$ that the Josephson-coupled nature of these materials is expected to manifest itself prominently.

After this phenomenological treatment, we present a full-fledged microscopic calculation of the critical field for layered compounds. This calculation begins in Sec. III, where we present a model Hamiltonian for layered compounds that includes free-electron propagation within each layer, tunneling of the electrons between the layers, an intralayer BCS-type pairing interaction, the effects of the magnetic fields on the electron spins, and both potential (spin-independent) and spin-orbit scattering within the layers. In Sec. IV, we use this model to calculate H_{c2} for all interlayer tunneling strengths. The results of this calculation are quite complicated due to their generality. However, based on the insights gained from our results using the phenomenological LD theory, we may gain considerable understanding of the predicted behavior by investigating those values of the material parameters for which the upper critical field behaves anomalously, i.e., with a temperature dependence of $H_{c2\parallel}$ that rises faster with decreasing temperature than in the case of an ordinary type-II superconductor.

In Sec. V, we examine the behavior expected in the temperature region near T_c. We find that in the dirty limit for electron propagation within the layers, the interesting region of the material parameters is obtained when the electrons scatter many times in a given layer before tunneling to an adjacent layer. Under these conditions, it is found that the upper critical field is determined by the solution of a single eigenvalue equation (related to the LD equation), which is of the form of a Schrödinger equation with both anharmonic and a periodic potential. The solution of this eigenvalue equation is discussed in detail in Sec. VI. In Sec. VII, we focus on the case when the field is parallel to the layers and find that for large spin-orbit scattering rates the equation for $H_{c2\parallel}(T)$ reduces to the usual pair-breaking form, with a pair-breaking parameter that depends in a complicated fashion upon the magnetic field strength. It is also found that in practice the Chandrasekhar-Clogston limit may be greatly exceeded in layered compounds if the spin-orbit scattering rate is extremely large, just as one would expect when the limits due to the usual orbital effects are ineffective.

Finally, in Sec. VIII, our results are discussed in light of the available experimental work on the critical fields of layered compounds.

II. PHENOMENOLOGICAL LAWRENCE-DONIACH MODEL

In terms of the order parameter $\Psi_j(\vec{r})$ for the position $\vec{r}$ in the jth layer, we write the Lawrence-Doniach free-energy functional in gauge-invariant form,

$$\mathfrak{F}_{\mathrm{LD}} = \int d^2r\, s \sum_j \Big[\alpha |\Psi_j(\vec{r})|^2 + \tfrac{1}{2}\beta |\Psi_j(\vec{r})|^4 + (1/2m)|(-i\vec{\nabla} - 2e\vec{A})\Psi_j(\vec{r})|^2 + (1/8\pi)|\vec{H}(\vec{r}) - \vec{H}_a(\vec{r})|^2 + \eta \left| \Psi_{j+1}(\vec{r}) \exp\left(-2ie\int_{js}^{(j+1)s} A_z\, dz\right) - \Psi_j(\vec{r}) \right|^2 \Big], \tag{3}$$

where

$$\alpha = [2m\xi^2(T)]^{-1} ,$$

$$\beta = 7\zeta(3)/2mNT_c\pi^3\tau\xi^2(0)$$

are the usual GL parameters in the dirty limit, η is the interlayer coupling parameter due to the Josephson tunneling of electron pairs, and $\vec{H}$ is the local magnetic field which is assumed constant and equal to H_a since we are only interested in calculating H_{c2}. $\vec{A}$ and A_z are the magnetic vector potentials parallel and perpendicular to the layers, respectively, and $\vec{\nabla}$ is the gradient operator parallel to the layers.

Equation (3) has been previously used by Yamaji,[14] for the case $A_z = 0$ to calculate the effect of fluctuations. It describes the free energy of a system of metallic layers, indexed by j, which obey the two-dimensional GL equations and are coupled by Josephson tunneling. Upon variation of Eq. (3) with respect to Ψ^*, and Fourier series transformation with respect to the variables perpendicular to the layers, we have

$$\{\alpha + (1/2m)(-i\vec{\nabla} - 2e\vec{A})^2 + 2\eta[1 - \cos(q_z s - 2eA_z s)]\}\Psi = 0 , \tag{4}$$

where we have neglected the term of order $|\Psi|^2\Psi$, which has no influence on $H_{c2}(T)$. Using the gauge

$$(\vec{A}, A_z) = H(0, x\cos\theta, -x\sin\theta) , \tag{5}$$

we have the one-dimensional Schrödinger equation with both an harmonic and a periodic potential,

$$\left\{\frac{1}{2m}\left[\frac{-d^2}{dx^2} + \left(2eHx\cos\theta\right)^2\right] + \frac{1}{Ms^2}[1 - \cos(q_z s + 2eHs\,x\sin\theta)]\right\}\Psi = -\alpha\Psi , \tag{6}$$

where we have identified $\eta = (2Ms^2)^{-1}$ for comparison with the results of anisotropic GL theory.

To calculate H_{c2}, we set $-\alpha$ equal to the lowest eigenvalue of Eq. (6), which occurs for $q_z = 0$ and determines the highest field for which a nontrivial solution to Eq. (4) exists. We observe that for the field perpendicular to the layers ($\theta = 0$), Eq. (6) leads to the GL result for a bulk type-II superconductor, $H_{c2\perp} = \Phi_0/2\pi\xi^2(T)$. For H parallel to the layers, Eq. (6) reduces to Mathieu's equation

$$\left(-\frac{1}{2m}\frac{d^2}{dx^2} + \frac{1}{Ms^2}[1 - \cos(2eHxs)]\right)\Psi = -\alpha\Psi . \tag{7}$$

For small magnetic field $[H \ll (m/M)^{1/2}/es^2]$ the cosine term may be expanded, the lowest eigenvalue of Eq. (7) is nearly proportional to the magnetic field, and we recover the expected anisotropic GL [Eq. (1)] result for $H_{c2\parallel}$. For large magnetic fields $[H \gg (m/M)^{1/2}/es^2]$, however, the electron pairs see the average of the periodic potential, and the lowest eigenvalue of Eq. (7) is nearly independent of the magnetic field. Carrying out a large magnetic field expansion, we find that the first-order corrections to the eigenvalue are of the order of H^{-2}, and obtain

$$H_{c2}^2(\pi/2, T) \cong \frac{m}{4Me^2s^4[1 - s^2/2\xi_z^2(T)]} , \tag{8}$$

where $\xi_z(T) = (m/M)^{1/2}\xi(T)$ is the GL coherence length perpendicular to the layers.

From Eq. (8), we note that if $\xi_z(0) < s/\sqrt{2}$, there is a temperature T^* defined by the relation

$$\xi_z(T^*) = s/\sqrt{2} , \tag{9}$$

at which the upper critical field parallel to the layers becomes infinite as the temperature is decreased. [Even if $\xi_z(0) \gtrsim s/\sqrt{2}$, the temperature dependence of H_{c2} is quite anomalous.] We interpret this extremely unusual behavior as an indication that at low temperature ($T < T^*$), the normal cores of the vortices fit between the layers, allowing the individual layers to remain superconducting in much larger magnetic fields than would be possible for an ordinary bulk type-II superconductor with the same GL coherence length. Moreover, our results strongly suggest that at low temperatures ($T < T^*$) layered compounds should behave as a series array of coupled Josephson junctions.

We note, however, that since the LD model is only valid near T_c, the above calculation is only qualitatively correct at best. Moreover, even though the normal cores of the vortices may indeed fit between the layers, the divergence of H_{c2} at T^* is clearly unphysical and results since any effect of a magnetic field on the superconductivity in the individual layers is completely neglected in the simple LD theory. The most obvious limitation for such thin layers is Pauli paramagnetic limiting as modified by spin-orbit scattering. In order to correct these shortcomings of the LD theory, it is necessary to carry out a calculation of H_{c2} using microscopic theory. Such a calculation is carried out in Secs. III and IV.

III. MODEL HAMILTONIAN

As a first step in developing a microscopic theory of H_{c2}, we construct a model Hamiltonian for the superconductivity of layered compounds. We define the field $\psi_{j\sigma}(\vec{r})$ corresponding to an electron with spin σ at position $\vec{r}$ in the jth layer in terms of the appropriate annihilation operator

$$\psi_{j\sigma}(\vec{r}) = (As)^{-1/2}\sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} a_{j\sigma}(\vec{k}) , \tag{10}$$

where A is the area of a layer, assumed the same for all layers, and sufficiently large so that boundary effects can be neglected. We assume periodic boundary conditions with regard to the layer indexes. The creation and annihilation operators obey the usual fermion anticommutation relations, and the field operators obey

$$\{\psi_{j\sigma}(\vec{r}),\ \psi^{\dagger}_{j'\sigma'}(\vec{r}\,')\}=s^{-1}\delta_{jj'}\delta_{\sigma\sigma'}\delta^{(2)}(\vec{r}-\vec{r}\,')\ ,$$
$$\{\psi_{j\sigma}(\vec{r}),\ \psi_{j'\sigma'}(\vec{r}\,')\}=0\ . \tag{11}$$

In terms of the field ψ, the Hamiltonian we shall consider is of the form

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_T+\mathcal{H}_{\rm imp}+\mathcal{H}_{\rm BCS}\ . \tag{12}$$

In Eq. (12), $\mathcal{H}_0$ is the single-particle Hamiltonian for an electron in the presence of a magnetic field, and is given by

$$\mathcal{H}_0=\int d^2r\, s\sum_{j\sigma}\Big[\psi^{\dagger}_{j\sigma}(\vec{r})\times\Big(-\frac{1}{2m}(\vec{\nabla}-ie\vec{A})^2-\mu_B\overleftrightarrow{\sigma}\cdot\vec{H}\Big)\psi_{j\sigma}(\vec{r})\Big]\ , \tag{13}$$

where μ_B is the Bohr magneton and $\overleftrightarrow{\sigma}$ is the Pauli spin matrix. The next term in the Hamiltonian, $\mathcal{H}_T$, is of the form

$$\mathcal{H}_T=\frac{J}{2}\int d^2r\, s\sum_{j\sigma}\Big[\psi^{\dagger}_{j\sigma}(\vec{r})\psi_{j+1,\sigma}(\vec{r})\times\exp\Big(-ie\int_{js}^{(j+1)s}A_z dz\Big)+\text{H. c.}\Big]\ , \tag{14}$$

where H. c. indicates the Hermitian conjugate. $\mathcal{H}_T$ is the gauge-invariant tunneling Hamiltonian and serves to couple a given layer to the two adjacent layers. The tunneling energy J is assumed independent of layer index and position in the layers.

The term in the Hamiltonian denoted by $\mathcal{H}_{\rm imp}$ is due to the presence of impurities in the layers, and is of the form

$$\mathcal{H}_{\rm imp}=\int d^2r\int d^2r'\, s^2\sum_{jl\sigma}\psi^{\dagger}_{j\sigma}(\vec{r})V_{jl}(\vec{r},\vec{r}\,')\psi_{l\sigma}(\vec{r}\,')\ , \tag{15}$$

where the scattering potential $V_{jl}(\vec{r},\vec{r}\,')$ is given by

$$\begin{aligned}V_{jl}(\vec{r},\vec{r}\,')&=s^{-1}\delta_{jl}\sum_n\int d^2p\int d^2q(2\pi)^{-4}\\&\quad\times\exp\{i\vec{p}\cdot[\tfrac{1}{2}(\vec{r}+\vec{r}\,')-\vec{R}^j_n]+i\vec{q}\cdot(\vec{r}-\vec{r}\,')\}\\&\quad\times(V_1+iV_{\rm so}\hat{p}\times\hat{q}\cdot\overleftrightarrow{\sigma})\\&=s^{-1}\delta_{jl}V_j(\vec{r},\vec{r}\,')\ ,\end{aligned} \tag{16}$$

and where $\vec{R}^j_n$ is the position of the nth impurity in the jth layer, $\hat{p}$ and $\hat{q}$ are unit vectors on the Fermi surface, and V_1 and $V_{\rm so}$ are the contributions to the scattering due to spin-independent and spin-orbit scattering, respectively. This term describes the scattering of an electron in a given layer due to the presence of impurities and is analogous to the term used by Abrikosov and Gorkov.[15] We have only included scattering within a given layer and have therefore completely neglected the scattering process that might take place during the tunneling from one layer to the next. Physically this implies we have restricted ourselves to the "clean limit" for propagation perpendicular to the layers.

The final term in the Hamiltonian is the BCS-type electron-electron interaction responsible for superconductivity, which we write as

$$\mathcal{H}_{\rm BCS}=\frac{\lambda s}{2}\sum_{j\sigma}\int d^2r\,\psi^{\dagger}_{j\sigma}(\vec{r})\psi^{\dagger}_{j,-\sigma}(\vec{r})\psi_{j,-\sigma}(\vec{r})\psi_{j\sigma}(\vec{r})\ , \tag{17}$$

which is the appropriate analog of the BCS pairing interaction due to the electron-phonon interaction.[16] The coupling constant λ is negative, as the interaction is attractive, and we assume that only electrons with energies within a narrow range of the Fermi energy may participate in the interaction. We note that this term in the Hamiltonian only pairs electrons of opposite spin and momentum in the same layer. We neglect pairing of electrons in different layers, within the spirit of the BCS theory for bulk superconductors, where the interaction is assumed to be pointlike.

Thus, this model describes a series of "two-dimensional" superconductors, coupled only through interlayer electron tunneling. As the tunneling energy J goes to zero, we might expect some problems to arise, as it has been shown that in the strict sense there is no long-range order in two-dimensional systems.[17] However, as long as J is finite, even though possibly very small, there will be sufficient coupling to allow for long-range order, and this model should have some validity. This conclusion has been reached by Tsuzuki[18] using a LD-type theory, and also by Gerhardts.[3] The arguments are similar for this model.

IV. CALCULATION OF $H_{c2}(\theta,T)$

We now calculate the upper critical field within the framework of our model of "two-dimensional" BCS-like superconductors coupled by electron tunneling between adjacent layers. We are principally interested in those values of the parameters of the theory for which $H_{c2}(\frac{1}{2}\pi,T)$ is anomalously large. In order to fully characterize such regions, we make no limitations upon the magnitude of any of the parameters, other than to assume that the dirty limit applies for electron propagation in the layers, and that the spin-orbit scattering rate is much less than the total scattering rate. In particular, we would like to determine those values of the interlayer coupling strength J for which $H_{c2}(\frac{1}{2}\pi,T)$ behaves anomalously and curves upward with decreasing temperature, as was found in the vicinity of T^* in the LD model discussed in Sec. II.

We define the temperature Green's functions in the usual way. For example,

$$G_{ij}^{\alpha\beta}(\vec{r},\tau;\vec{r}',\tau') = \frac{-\langle T_\tau[\psi_{i\alpha}(\vec{r},\tau)\psi^\dagger_{j\beta}(\vec{r}',\tau')\mathcal{S}]\rangle}{\langle\mathcal{S}\rangle} , \quad (18)$$

where

$$\mathcal{S} = T_\tau \exp\left(-\int_0^{T^{-1}} \mathcal{H}_{\mathrm{BCS}}(\tau)\,d\tau\right) , \quad (19)$$

and the operators are all in the Heisenberg representation. In Eq. (18), the averages indicated are statistical averages in the grand canonical ensemble. From Eqs. (18) and (19), we see that the normal-state Green's function G^n, which describes the propagation of an electron in the absence of the pairing interaction responsible for superconductivity, is obtained from G by setting $\lambda = 0$. For the Hamiltonian described in Sec. III with λ set equal to zero, the equation of motion for the normal-state Green's function G^n is found to be

$$[i\omega + \vec{\nabla}^2/2m + \mu + \mu_B \overleftrightarrow{\sigma}\cdot\vec{H} - \tfrac{1}{2}J(\hat{\Delta}_{j+}+\hat{\Delta}_{j-})]G^n_{\omega\sigma jl}(\vec{r},\vec{r}') - s\sum_{j'}\int d^2r''\, V_{j'}(\vec{r},\vec{r}'')G^n_{\omega\sigma j'l}(\vec{r}'',\vec{r}') = s^{-1}\delta_{lj}\delta^{(2)}(\vec{r}-\vec{r}') , \quad (20)$$

where we have taken the usual Fourier series transformation with respect to the variables τ and τ', and μ is the chemical potential. In Eq. (20), we have defined the index raising and lowering operator to obey

$$\hat{\Delta}_{j\pm}\psi_{j\sigma}(\vec{r}) = \psi_{j\pm1,\sigma}(\vec{r}) . \quad (21)$$

The quantity G^n is then found from the normal-state Green's function in the absence of impurities, G^0, by the usual impurity-averaging technique. The Fourier transform of G^0 is found, from Eq. (20), to be

$$G^0_{\omega\sigma}(\vec{k},k_z) = (i\omega_- - \xi_{\vec{k}} - J\cos k_z s)^{-1} , \quad (22)$$

where

$$\omega_\pm = \omega \pm i\mu_B \overleftrightarrow{\sigma}\cdot\vec{H} ,$$

and

$$\xi_{\vec{k}} = \vec{k}^2/2m - \mu .$$

We define the total scattering time τ by

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_{\mathrm{so}}} , \quad (23)$$

where

$$\frac{1}{\tau_1} = nN_{\mathrm{2D}}(0)\int_0^{2\pi} d\theta\, V_1^2(\theta) \quad (24)$$

and

$$\frac{1}{\tau_{\mathrm{so}}} = nN_{\mathrm{2D}}(0)\int_0^{2\pi} d\theta\, \sin^2\theta\, V^2_{\mathrm{so}}(\theta) \quad (25)$$

are the two-dimensional spin-independent and spin-orbit scattering times, respectively, n is the number of impurity sites per unit area of a layer, and $N_{\mathrm{2D}}(0) = m/2\pi$ is the two-dimensional density of states for a single electron spin. The diagrams corresponding to the lowest-order impurity-averaging processes are shown in Fig. 1.

Assuming $E_F\tau \gg 1$, the only diagrams in Fig. 1 that contribute significantly to the electron lifetime are those of the form shown in Figs. 1(b), 1(e), and 1(f), in which the electrons scatter twice off the same impurity site, and in which there are no crossed impurity averaging lines, such as shown in Fig. 1(g). Diagrams with an odd number of impurity scattering potentials do not contribute to the electron lifetime, but serve to redefine the Fermi energy. We therefore keep only the diagrams of the type shown in Figs. 2(a),

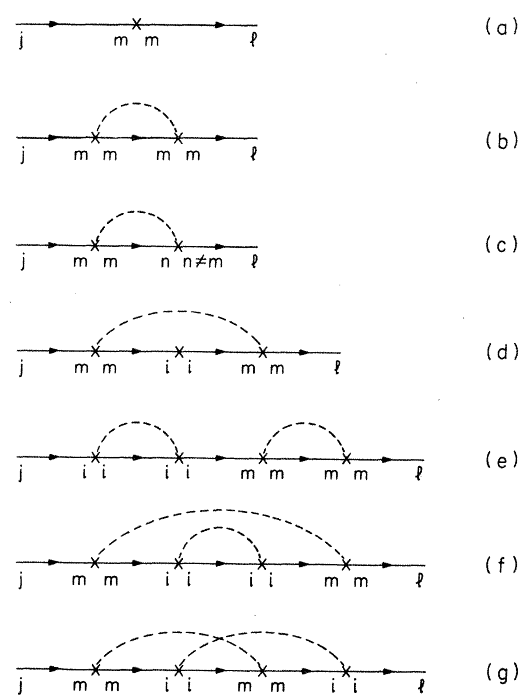

FIG. 1. Shown are typical diagrams contributing to the normal-state Green's function in the presence of impurities. The solid lines represent the normal-state Green's functions in the presence of tunneling but in the absence of scattering, and the dashed curves refer to the simultaneous averaging of the two indicated impurity sites.

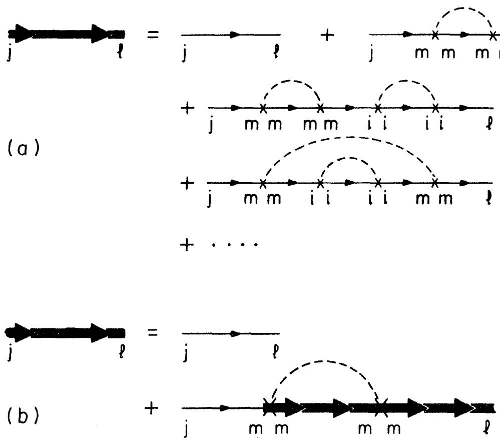

FIG. 2. (a) Diagrams to fourth order in the impurity potential that make a significant contribution to the electron lifetime. (b) Diagrammatic representation of the integral equation for the normal-state Green's function in the presence of both tunneling and scattering (thick line) that results from summing the series indicated in Fig. 2(a).

which, when summed, give the integral equation shown diagramatically in Fig. 2(b).

Taking the Fourier transform of this equation with respect to the variables parallel to the layers, and the Fourier series transformation of the variables perpendicular to the layers, we find that the normal-state Green's function G^n can be expressed in the usual mass operator form,

$$[G^n_{\omega\sigma}(\vec{k}, k_z)]^{-1} = [G^0_{\omega\sigma}(\vec{k}, k_z)]^{-1} - \Sigma_\omega(\vec{k}, k_z) \ , \tag{26}$$

where the self-energy $\Sigma_\omega(\vec{k}, k_z)$ is given by

$$\Sigma_\omega(\vec{k}, k_z) = ns \int \frac{d^2\vec{p}}{(2\pi)^2} \int_{-\pi/s}^{\pi/s} \frac{dp_z}{2\pi} \times [V_1 + iV_{so}(\hat{p}\times\hat{k})\cdot\overleftrightarrow{\sigma}] \times G^n_{\omega\sigma}(\vec{p}, p_z)[V_1 + iV_{so}(\hat{k}\times\hat{p})\cdot\overleftrightarrow{\sigma}] \ . \tag{27}$$

In Eq. (27), the integral with respect to p_z is due to the tunneling of an electron from a given layer to any other layer and back, scattering an even number of times in any of the layers to which it propagates. From the structure of the self-energy, it is seen that the integration with respect to p_z serves only to renormalize the Fermi energy, as it is only the imaginary part of the self-energy that gives rise to an electron lifetime. We therefore obtain

$$G^n_{\omega\sigma}(\vec{k}, k_z) = (i\tilde{\omega}_- - \xi_{\vec{k}} - J\cos k_z s)^{-1} \ , \tag{28}$$

where the renormalized frequency $\tilde{\omega}_-$ is given by

$$\tilde{\omega}_\pm = \omega\left(1 + \frac{1}{2\tau|\omega|}\right) \pm i\mu_B \overleftrightarrow{\sigma}\cdot\vec{H} \ . \tag{29}$$

Thus, the effect of impurities on the single-electron normal-state Green's function for a layered superconductor is completely analogous to that for impurity scattering in a bulk superconductor, except for the definitions of the scattering times. The simultaneous effects of impurity scattering and interlayer tunneling upon the normal-state Green's function appear to be independent, the impurity scattering serving only to renormalize the frequency, and the tunneling processes giving rise to the single-electron states of the tight-binding form with regard to motion perpendicular to the layers.

In order to calculate the upper critical field, we assume, as in the calculations of Maki[19] and of Werthamer, Helfand, and Hohenberg (WHH),[20] that H_{c2} is given by a supercooling field, which corresponds to the points at which the superconducting state can form with an arbitrarily small gap. We therefore form the linearized Gorkov gap equation for a layered superconductor, keeping only the lowest-order term in the expansion in power of the gap Δ, and are led to the result

$$\Delta^*(\vec{q}, q_z) = \frac{|\lambda| T}{2} \operatorname{Tr} \sum_\omega \int_{-\pi/s}^{\pi/s} \frac{dk_z}{2\pi} \int \frac{d^2k}{(2\pi)^2} \times \langle G^n_{\omega\sigma}(\vec{k}, k_z)\, G^n_{-\omega,-\sigma}(\vec{q} - \vec{k}, q_z - k_z)\rangle\, \Delta^*(\vec{q}, q_z) \ , \tag{30}$$

where the trace implies the sum over the two possible spin configurations, and the average is over the impurity sites. An equation for the upper critical field can be found from Eq. (3) by making the replacement

$$(\vec{q}, q_z) \to (\vec{q} - 2e\vec{A}, q_z - 2eA_z) \ , \tag{31}$$

which is valid in the dirty limit and where the gauge is given by Eq. (5).

Since we have already found the effect of impurities upon the single-particle normal-state Green's function, we need now only calculate the simultaneous effect of impurities upon the product of two Green's functions. Thus, we average one impurity site in the expansion of one Green's function with a site in the expansion of the other Green's function. The internal lines are the normal-state Green's functions in the presence of impurities, as given by Eq. (28). We retain only the ladder diagrams, as the remaining diagrams contain crossed impurity averaging lines, and are thus negligible for $E_F\tau \gg 1$. We thus have the integral equation shown diagramatically in Fig. 3.

For the case of bulk type-II superconductors, the analogous integral equation has been solved by Maki[19] and by WHH.[20] The general procedure we use is similar to that of WHH, and is discussed more fully in the Appendix. In the limit that the spin-orbit scattering rate is much less than the total scattering rate ($\tau^{-1} \gg \tau_{so}^{-1}$), and in the dirty limit for the electron propagation in the layers (i.e., $l \ll \xi_0$, where $l = v_F\tau$ is the mean free path in the layers, and ξ_0 is the BCS coherence length in the layers, respectively), we have the implicit equation for $H_{c2}(\theta, T)$

$$\ln\left(\frac{T}{T_{c0}}\right) = 2\pi T \sum_{\omega_n > 0} \left(\frac{(\omega_+^* + \omega_-^* + a_+ + a_-)/2 + b}{(\omega_+^* + a_+)(\omega_-^* + a_-) - b^2} - \frac{1}{\omega_n}\right) ,$$

where

$$\begin{aligned} b &= 1/3\tau_{so} , \\ a_\pm &= b + Q_\pm^2/2\tau , \\ \omega_\pm^* &= [\tilde{\omega}_\pm^2 + J^2(1 - \cos q_z s)/2]^{1/2} - 1/2\tau , \\ Q_\pm^2 &= \frac{[1 - J^2(1 - \cos q_z s)/4\tilde{\omega}_\pm^2]\, v_F^2 \vec{q}^2}{8\tilde{\omega}_\pm^2[1 + J^2(1 - \cos q_z s)/2\tilde{\omega}_\pm^2]^2} , \\ \tilde{\omega}_\pm^2 &= \left[\omega_n\left(1 + \frac{1}{2\tau|\omega_n|}\right) \pm iI\right]^2 , \end{aligned} \tag{32}$$

and where $I = \mu_B H$ contains the effect of the Pauli paramagnetism, $\omega_n = (2n+1)\pi T$ is the fermion Matsubara frequency, and the magnetic field is introduced as in Eq. (31). In Eq. (32), we have used the analogous BCS-type (or mean-field) relation for the zero-field transition temperature of the layered superconductors, which for $J \ll \omega_D$ is nearly independent of J (see Ref. 3),

$$|\lambda| N(0) \ln(2\gamma\omega_D/\pi T_{c0}) = 1 , \tag{33}$$

where $N(0) = m/2\pi s$ is the electron single-spin density of states for a layered superconductor, $\gamma = 1.78$, and ω_D is the Debye frequency.

In Eq. (32), we have made no restrictions upon the magnitude of the interlayer tunneling energy J. However, as we expect that the anomalous behavior of interest occurs only in the "decoupled" regime, we anticipate that J must be "small." (We also must establish the appropriate quantity to which J should be compared.) In particular, we wish to isolate those values of J and the other parameters for which $H_{c2}(\frac{1}{2}\pi, T)$ curves upward with decreasing temperature. We note that in contrast to the case for bulk type-II superconductors, here the choice of the dirty limit requires only that the coherence length in the layers be much larger than the mean free path, or more precisely $Q_\pm^2 \ll 1$. Unlike the dirty limit in the conventional theory, this assumption places no restrictions upon the total scattering rate relative to T_{c0}. However, since we expect that the materials of physical interest will satisfy the condition $\tau T_{c0} \ll 1$, in our subsequent discussion, we shall focus upon that limit. The case for $\tau T_{c0} \gg 1$ has been discussed elsewhere.[21]

V. THE UPPER CRITICAL FIELD NEAR THE ZERO-FIELD TRANSITION TEMPERATURE

From our results using the LD theory (Sec. II), very near T_{c0} we expect H_{c2} to behave like an ordinary anisotropic bulk superconductor, that is, with a temperature dependence $H_{c2}(T) \propto T - T_{c0}$. We therefore anticipate that a power series in $T - T_{c0}$ should provide a good expansion for H_{c2} in the vicinity of T_{c0}. Moreover, it is clearly the term quadratic in $T - T_{c0}$ that, to lowest order, will contain any of the usual effects predicted in Sec. II. In the LD theory, $H_{c2}(\frac{1}{2}\pi, T)$ can be shown to have a positive coefficient for the quadratic term in the power series expansion in $T - T_{c0}$, whereas for an ordinary bulk type-II superconductor this coefficient is negative. Thus, the sign of the quadratic term is a convenient indicator of anomalous behavior of $H_{c2}(\frac{1}{2}\pi, T)$.

To determine H_{c2} and to establish the values of the material parameters leading to anomalous behavior, we must first transform Eq. (32) back to position space with regard to the variables parallel to the layers. This is equivalent to rewriting Eq. (31) as

$$(\vec{q}, q_z) \to (-i\vec{\nabla} - 2e\vec{A}, q_z - 2eA_z) . \tag{34}$$

We must then find the lowest eigenvalue of the resulting operator equation, which occurs for $q_z = 0$. We observe that the transformed Eq. (32) is a function of two separate operators $\hat{L}^\pm = a_\pm + \omega_\pm^*$, where $a_\pm$ and $\omega_\pm^*$ are themselves operators due to the transformation. We therefore must solve the eigenvalue equations

$$\hat{L}^\pm \phi_\pm^0 = E_\pm^0 \phi_\pm^0 , \tag{35}$$

where $E_\pm^0$ and $\phi_\pm^0$ are the lowest eigenvalues and eigenfunctions of the respective eigenvalue equations.

The operators $\hat{L}^\pm$ may each be broken into two parts: one that is of the form of the Schrödinger harmonic oscillator, giving rise to an eigenvalue proportional to H; and one that may be treated as a perturbation, giving a correction to the eigenvalue of order H^2. Equation (32) may now be solved for the coefficient of the quadratic term in the $T - T_{c0}$ expansion for H_{c2}. The solution for all values of the parameters is given elsewhere.[21] For $\tau T_{c0} \ll 1$ and for the field parallel to the layers, we have

$$T_{c0}^2 \frac{\partial^2 H_{c2}(\frac{1}{2}\pi, T)}{\partial T^2}\bigg|_{T_{c0}} = T_{c0} \frac{\partial H_{c2}(\frac{1}{2}\pi, T)}{\partial T}\bigg|_{T_{c0}} \left[\left[1 - \frac{56\zeta(3)}{\pi^4}\right] - \frac{2\tau T_{c0}}{\pi}\left(\frac{1}{(J\tau)^2} - 7\right) + \frac{2^8 \mu_B^2 g(\tau_{so})}{\pi^4 (s v_F e J \tau)^2}\right], \tag{36}$$

where

$$g(\tau_{so}) = \sum_{n=0}^{\infty} (2n+1)^{-2}[2n+1+2/3\pi\tau_{so}T_{c0}]^{-1},$$

$$\left.\frac{\partial H_{c2}(\frac{1}{2}\pi, T)}{\partial T}\right|_{T_{c0}} = \frac{-8}{\pi e J s v_F \tau} .$$

The right-hand side of Eq. (36) separates naturally into three parts: the first two terms in the brackets together comprise a negative contribution to the curvature of H_{c2} and represent the usual corrections to the GL result obtained from the presence of Pauli paramagnetism and spin-orbit scattering, and also tends to decrease the curvature of H_{c2} as it does for a bulk superconductor. The middle term, however, is due to the layered structure of the materials in question and can be of either sign, depending upon the magnitude of $(J\tau)^2$. Inspection of Eq. (36) shows that the quadratic term in the expansion for $H_{c2}(\frac{1}{2}\pi, T)$ in powers of $T - T_{c0}$ can be positive only for $(J\tau)^2 < \frac{1}{7}$, and then only for certain values of the remaining parameters. [We remark that similar results[21] are obtained for $\tau T_{c0} \gg 1$. In this case, the quadratic term can be positive only if $(J/T_{c0})^2 < \frac{40}{7}$.]

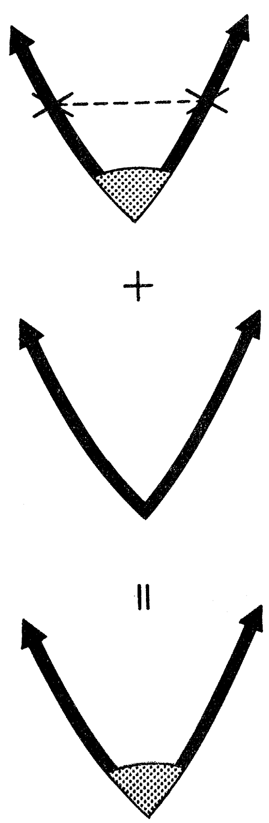

FIG. 3. Digrammatic representation of the integral equation for the product of two Green's functions in the presence of impurities.

Inspection of the above results indicates that the upward curvature of $H_{c2}(\frac{1}{2}\pi/T)$ predicted by our calculations is most pronounced when the Pauli paramagnetic limiting is highly quenched by spin-orbit scattering. Therefore, since $\tau_{so} \geqq \tau$ always, the most promising case for obtaining an upward curvature is when $\tau T_{c0} \ll 1$ and $(J\tau)^2 \ll 1$, i.e., in the extremely dirty limit and when the electrons scatter many times in a given layer before tunneling to an adjacent layer. In the opposite case when $\tau T_{c0} \gg 1$, $g(\tau_{so})$ is of order 1 and cannot be made small by even the maximum allowable spin-orbit scattering rate.

With the favorable conditions, we may rewrite Eq. (32) in terms of the usual digamma functions

$$\ln\left(\frac{T}{T_{c0}}\right) + \frac{1}{2}\left[\left(1 - \frac{b}{(b^2 - I^2)^{1/2}}\right)\psi\left(\tfrac{1}{2}+\rho_+\right) + \left(1 + \frac{b}{(b^2 - I^2)^{1/2}}\right)\psi\left(\tfrac{1}{2}+\rho_-\right)\right] - \psi\left(\tfrac{1}{2}\right) = 0, \tag{37}$$

where

$$\rho_\pm = (2\pi T)^{-1}\,[b + \epsilon \pm (b^2 - I^2)^{1/2}], \tag{38}$$

and ϵ is the lowest eigenvalue of the equation

$$\left[D\left(\frac{-d^2}{dx^2} + (2eHx\cos\theta)^2\right) + J^2\tau[1 - \cos(2eHxs\sin\theta)]\right]\varphi = 2\epsilon\varphi. \tag{39}$$

For strong spin-orbit scattering, $b \gg I$, which is necessary to give a pronounced upward curvature of of $H_{c2}(\pi/2, T)$, Eq. (37) reduces to

$$\ln\left(\frac{T}{T_{c0}}\right) + \psi\left(\frac{1}{2} + \frac{\alpha}{2\pi T}\right) - \psi\left(\tfrac{1}{2}\right) = 0 , \tag{40}$$

where the pair-breaking parameter α is given by

$$\alpha = \epsilon + \tfrac{3}{2}\tau_{so}I^2 . \tag{41}$$

Thus, for $(J\tau)^2 \ll 1$ and $\tau T_{c0} \ll 1$, we obtain an expression for $H_{c2}(\theta, T)$ differing from that for a bulk superconductor only in terms of the eigenvalue ϵ. This eigenvalue is not a simple function of the relevant parameters, however, and we study its behavior in the following section.

VI. THE EIGENVALUE EQUATION

In order to find $H_{c2}(\theta, T)$ as given by Eq. (37), we must first find the lowest eigenvalue of the eigenvalue equation, Eq. (39). We observe that this is a one-dimensional Schrödinger equation with both an harmonic and a periodic potential.[22] For the field perpendicular to the layers, we have only the harmonic potential, and for the field parallel to the layers, only the periodic potential. Since for the periodic potential alone, a solution valid for all values of H cannot readily be expressed in terms of a finite set of elementary functions, we anticipate that for arbitrary angles of the magnetic field, the best analytic solution will be an expansion for small magnetic field strengths, and one for large field strengths.

Near T_{c0}, H_{c2} is small, and the eigenvalue may be expanded in powers of H to give

$$\epsilon = DeHa(\theta) - \frac{(eHs^2J)^2\tau\sin^4\theta}{16\,a^2(\theta)} + \frac{(eHs^2)^3J^2\tau\sin^6\theta}{384\,a^3(\theta)}\left(4 - \frac{7J^2s^2\tau\sin^2\theta}{2Da^2(\theta)}\right) + O(H^4)\ , \tag{42}$$

where

$$a(\theta) = [\cos^2\theta + (J^2\tau s^2/2D)\sin^2\theta]^{1/2} \tag{43}$$

is the anisotropy factor. We observe that the term linear in H is of the form expected for a dirty, anisotropic bulk type-II superconductor, and that as $\theta \to 0$, the other terms disappear. As $\theta \to \frac{1}{2}\pi$, the expansion is in agreement with the low-field expansion of the eigenvalue of the Mathieu equation.[23]

The "high-field" expansion is more subtle. If one is interested in the behavior of ϵ near $\theta = \frac{1}{2}\pi$, then one might be tempted to treat the periodic potential as the unperturbed potential and treat the harmonic term as a perturbation, using the high-field expansions for the periodic eigenfunctions as the basis. This approach turns out to be unacceptable, however, as the perturbation is unbounded, and therefore has regions where it exceeds the unperturbed potential, except exactly at $\theta = \frac{1}{2}\pi$. Instead, we treat the periodic part of the potential as the perturbation for all angles. A simple expansion parameter is not readily apparent, however. Carrying out the calculations, we obtain

$$\epsilon = DeH\cos\theta + \frac{J^2\tau}{2}(1 - e^{-\chi/2}) - \frac{J^4\tau^2 e^{-\chi}}{8DeH\cos\theta}\int_0^\chi dy\,\frac{\cosh y - 1}{y} + O\left[\left(\frac{J^2\tau s^2}{D}\right)^3\right]\ , \tag{44}$$

where

$$\chi = eHs^2\sin^2\theta/\cos\theta\ . \tag{45}$$

We observe that Eq. (44) is an expansion in powers of $J^2\tau s^2\tan^2\theta/D$ for $\chi \ll 1$, and in powers of $J^2\tau/D$ $(eHs\sin\theta)^2$ for $\chi \gg 1$. It is convergent for all angles. In particular, as $\theta \to 0$, $\epsilon \to DeH$, the bulk isotropic result. As $\theta \to \pi/2$, we have

$$\epsilon \to \frac{J^2\tau}{2} - \frac{J^4\tau^2}{16Ds^2e^2H^2} + O(H^{-3})\ , \tag{46}$$

which is the result of the high-field solution of the Mathieu equation.[23] We further note that Eq. (44), if expanded in powers of H, is in agreement with Eq. (42) expanded in powers of $J^2\tau s^2/D$. That Eq. (44) can be considered to be the high-field expansion is due to the fact that it reduces to the high-field form of the eigenvalue for $\theta = \frac{1}{2}\pi$, although as $\theta \to 0$, the form of the solution is the same with both perturbation techniques.

VII. THE UPPER CRITICAL FIELD PARALLEL TO THE LAYERS

From Eq. (44) we see that the eigenvalue is nearly proportional to H for $\theta \neq \frac{1}{2}\pi$. Therefore, it is only for the field parallel to the layers that the behavior of H_{c2} is strongly anomalous. We now examine this limit in detail.

In this limit, the eigenvalue equation may be written as a function of a single parameter,

$$\left(\frac{-h^2}{2}\frac{d^2}{dy^2} + (1 - \cos 2y)\right)\varphi = \left(\frac{2\epsilon}{J^2\tau}\right)\varphi\ , \tag{47}$$

where

$$h = eHs^2(2D/J^2\tau s^2)^{1/2} \tag{48}$$

is a reduced field. The eigenvalue ϵ may be written in terms of a dimensionless function f defined by

$$f(h) = 2\epsilon/rT_{c0}\ , \tag{49}$$

where $r = J^2\tau/T_{c0}$ is a parameter gauging the interlayer coupling strength and was used previously by the authors[2] to distinguish the regions of two- and three-dimensional behavior in the fluctuation regime above T_{c0}. In order to compare our results with those for a bulk anisotropic type-II superconductor, we make the identification

$$m/M = J^2\tau s^2/2D\ , \tag{50}$$

where m/M is the ratio of the GL effective pair masses.

In Fig. 4, we have plotted the function $f(h)$. For $h \ll 1$, $f \sim h$, so that for small magnetic fields, ϵ and $H_{c2}(\frac{1}{2}\pi, T)$ reduce to the familiar GL result. For $h \gg 1$, however, $f \sim 1$, which characterizes the "decoupled" behavior, that is, when the vortices are centered between the layers and do not contribute significantly to the destruction of superconductivity in the layers. Since the parallel upper critical field of a thin film depends upon the thickness of the film, the field-independent region of the eigenvalue in the limit as $r \to 0$ corresponds to the upper critical field we might expect for an "infinitely thin," or more precisely, purely Pauli paramagnetism-limited film.[24]

If we now neglect the effects of Pauli paramagnetism and spin-orbit scattering (or, equivalently, assume that the spin-orbit scattering rate is infinite), we then may use the pair-breaking equation, Eq. (40), combined with Eq. (47) to obtain a more accurate equation for T^*, the temperature at which $H_{c2}(\frac{1}{2}\pi, T)$ would become infinite in the absence of these effects,

$$\ln(T^*/T_{c0}) + \psi(\tfrac{1}{2} + rT_{c0}/4\pi T^*) - \psi(\tfrac{1}{2}) = 0 \ . \qquad (51)$$

In the insert of Fig. 5, we have plotted T^*/T_{c0} as a function of r. We observe that for $r < \pi/\gamma$, $T^* > 0$, whereas in the LD theory of Sec. II, $T^* > 0$ for $r < 8/\pi$.

A complete characterization and interpretation of the types of critical field curves predicted by our model would be quite tedious owing to the relatively complicated form of the results when the orbital effects, Pauli paramagnetism, and spin-orbit scattering all simultaneously affect the behavior. In order to gain some insight, however, we have attempted to identify the values of the material parameters for which one or another of the various factors influencing $H_{c2}(\frac{1}{2}\pi)$ dominate, and also those values of the parameters for which clearly anomalous H_{c2} behavior is expected.

For economy of exposition we restrict ourselves to the physically interesting case of strong spin-orbit scattering $\tau_{so}T_{c0} \ll 1$. Moreover, we further restrict ourselves, at least initially, to a discussion of the value of the critical field at $T = 0$, $H_{c2}(\frac{1}{2}\pi, 0)$. In this case, the pair-breaking equation leads to the following results

$$f(h_0) + \tfrac{3}{4}\tau_{so} T_{c0} r \alpha^2 h_0^2 = f(h_0) + \zeta h_0^2 = \pi/\gamma r, \qquad (52)$$

where

$$\alpha = (M/m)^{1/2} \mu_B / eD \qquad (53)$$

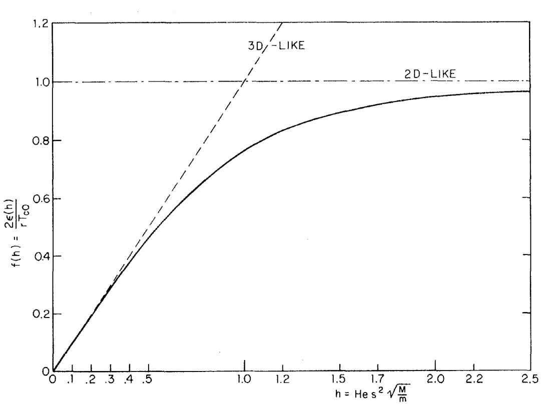

FIG. 4. Plot of the dimensionless eigenvalue $2\epsilon(h)/rT_{c0}$ of the eigenvalue equation for the field parallel to the layers as a function of the reduced field $h = H\, es^2(M/m)^{1/2}$. The broken lines are the results for an anisotropic bulk superconductor and for the completely decoupled limit.

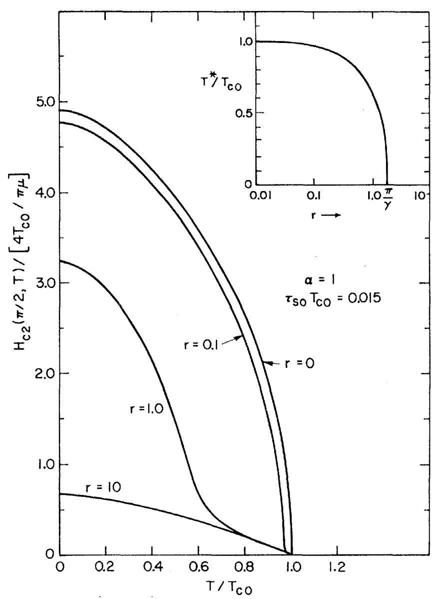

FIG. 5. Plot of $H_{c2}(\frac{1}{2}\pi, T)/H_P$ as a function of T/T_{c0} for $\alpha = 1$, $\tau_{so}T_{c0} = 0.015$, and for various values of r. The $r = 0$ curve is the result for a purely Pauli-limited thin film. Insert: Plot of T^*/T_{c0} as a function of r. T^* is the temperature at which $H_{c2\parallel}$ would become infinite in the absence of Pauli paramagnetism and spin-orbit scattering.

is the appropriate anisotropic generalization of the pair-breaking parameter for Pauli paramagnetism, and $H_{c2}(\frac{1}{2}\pi, 0)$ is obtained from the value h_0 given by Eq. (52) using the definition of h given in Eq. (48).

From Eq. (52) it is clear that under these conditions $H_{c2}(\frac{1}{2}\pi, 0)$ depends on the two parameters r and ζ. Figure 6 shows the value of $H_{c2}(\frac{1}{2}\pi, 0)$ obtained from Eq. (52) as a function of ζ for various values of r. Figure 7 indicates the important factors governing $H_{c2}(\frac{1}{2}\pi, 0)$ under any given condition. The domains and boundaries depicted in this figure are established as follows.

From Fig. 4, we observe that the extrapolated curves corresponding to bulk anisotropic type-II behavior ($f = h$) and fully decoupled behavior ($f = 1$) become equal at $h = h_D \equiv 1$. That value of $H_{c2}(\frac{1}{2}\pi, 0)$ for which $h_0 = h_D$ therefore represents a crossover field separating the region of 3D-like bulk behavior from that of 2D-like behavior in which H_{c2} is purely Pauli limited as in a very thin film.

Since in Eq. (52) $H_{c2}(\frac{1}{2}\pi, 0)$ is determined by two terms, one depending upon Pauli paramagnetism and spin-orbit scattering and the other depending upon the field dependence of the orbital effects, we define the reduced field h_p to specify when these contributions to $H_{c2}(\frac{1}{2}\pi, 0)$ become equal. We thus choose h_p to satisfy

$$f(h_p) = \zeta h_p^2 \ . \qquad (54)$$

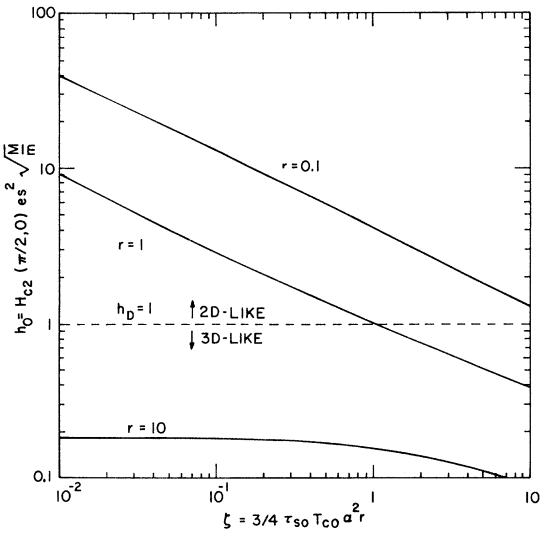

FIG. 6. Plot of the $h_0 = H_{c2}(\frac{1}{2}\pi, 0)\ es^2(M/m)^{1/2}$ as a function of $\zeta = \frac{3}{4}\tau_{so}T_{c0}\,\alpha^2 r$ for $r = 0.1$, 1, and 10. Also shown is the value $h_D = 1$, which distinguishes the region characteristic of a bulk anisotropic superconductor from that characteristic of a purely Pauli-limited thin film.

Thus, for $h > h_p$, the effects of Pauli paramagnetism and spin-orbit scattering are important in determining $H_{c2}(\frac{1}{2}\pi, 0)$, whereas for $h < h_p$, the orbital effects are important.

In addition, there is a reduced field h_a that distinguishes between the possible shapes of the $H_{c2}(\frac{1}{2}\pi, T)$ curves as a function of temperature. In the absence of Pauli paramagnetism and spin-orbit scattering effects, the anisotropic bulk superconductor would have an $H_{c2}(\frac{1}{2}\pi, 0)$ given by

$$h_a = \pi/\gamma r\ . \tag{55}$$

Since for strong spin-orbit scattering rates, $H_{c2}(\frac{1}{2}\pi, T)$ increases monotonically with decreasing temperature, if $h_0 > h_a$, then $H_{c2}(\frac{1}{2}\pi, T)$ would be enhanced above the curve for an ordinary bulk type-II superconductor with the same degree of anisotropy. Thus, the enhancing effects upon H_{c2} of a large spin-orbit scattering rate would outweigh the Pauli paramagnetism limiting. For $h < h_a$, $H_{c2}(\frac{1}{2}\pi, T)$ would lie below the curve for the bulk superconductor with the same anisotropy in the absence of paramagnetic effects, the enhancement due to strong spin-orbit scattering rates being outweighed by the Pauli paramagnetism limiting. For a given value of ζ, in order to determine which of these effects will dominate, we must solve for ζ in terms of h_a. Employing both Eq. (52) and Eq. (55), we find that ζ is given in terms of h_a by

$$\zeta = [h_a - f(h_a)]/h_a^2\ . \tag{56}$$

Examination of Fig. 7 reveals that the most interesting region of $H_{c2}(\frac{1}{2}\pi, 0)$ is for $h > h_p$ and for $\zeta(h_0) < \zeta(h_a)$, where the spin-orbit scattering enhancement is so strong that it causes $H_{c2}(\frac{1}{2}\pi, T)$ to greatly curve upward with decreasing temperature.

In order to display the $H_{c2}(\frac{1}{2}\pi, 0)$ values attainable for various values of r, in Fig. 6 we have plotted the h_0 versus ζ curves for three different r values. The dimensional crossover curve, $h_D = 1$, is also shown. For $r = 0.1$, $H_{c2}(\frac{1}{2}\pi, 0)$ is primarily determined by Pauli paramagnetism and spin-orbit scattering effects and is similar to the $H_{c2}(\frac{1}{2}\pi, 0)$ for a purely Pauli-limited thin film. For $r = 10$, $H_{c2}(\frac{1}{2}\pi, 0)$ lies generally in the region where Pauli paramagnetism and spin-orbit scattering are not important, and exhibits basically three-dimensional behavior. For $r = 1$, $H_{c2}(\frac{1}{2}\pi, 0)$ is in the intermediate region both with regard to dimensionality and with regard to the importance of the effects of Pauli paramagnetism and spin-orbit scattering.

In order to illustrate the dependence upon temperature of the effective dimensionality of the materials, in Fig. 5 we have plotted $H_{c2}(\frac{1}{2}\pi, T)$ versus T/T_{c0} for a fixed spin-orbit scattering rate $T_{so}T_{c0} = 0.015$, a fixed $\alpha = 1$, and for various values of r, including $r = 0$, which corresponds to a purely Pauli-

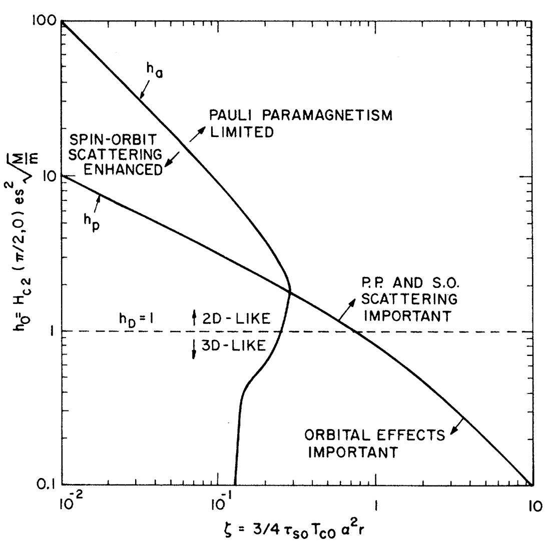

FIG. 7. Map of the regions of different physical significance of the reduced field $h_0 = H_{c2}(\frac{1}{2}\pi, 0)\ es^2(M/m)^{1/2}$. The boundaries of these regions are the curves h_p and h_a, which are functions of $\zeta = \frac{3}{4}\tau_{so}T_{c0}\alpha^2 r$. The reduced field h_p distinguishes the region where Pauli paramagnetism and spin-orbit scattering are more important than the orbital effects in determining $H_{c2}(\frac{1}{2}\pi, 0)$ from the region in which the opposite is true. The reduced field h_a distinguishes those $H_{c2}(\frac{1}{2}\pi, T)$ curves that rise more rapidly with decreasing temperature than an anisotropic bulk superconductor in the absence of Pauli paramagnetism and spin-orbit scattering does from those $H_{c2}(\frac{1}{2}\pi, T)$ curves in which the opposite is true.

limited thin film. We observe that the $r=10$ curve is indistinguishable from that of a bulk anisotropic type-II superconductor, and that the $r=0.1$ curve is very similar to that of a purely Pauli-limited thin film except in the region in temperature very near to T_{c0}, where the thin film curve goes to zero with infinite slope, whereas the $r=0.1$ curve goes to zero with finite slope. The $r=1$ curve is intermediate to the $r=10$ and $r=0.1$ curves, more closely approaching the curve characteristic of a bulk type-II superconductor for $T>T^*$, and more closely approaching the curve for a purely Pauli-limited thin film for $T<T^*$. The "dimensional crossover" behavior at T^* is thus clearly evident.

In Fig. 8, we have plotted $H_{c2}(\frac{1}{2}\pi, T)$ versus T/T_{c0} for $r=10$, for $\alpha=1$ and 5, and for various spin-orbit scattering rates. We observe that for $\alpha=1$, the shapes of the $H_{c2}(\frac{1}{2}\pi, T)$ versus T curves are relatively independent of spin-orbit scattering rate, as predicted by Figs. 6 and 7. For $\alpha=5$, however, the Chandrasekhar-Clogston limit can be considerably exceeded, and the effects of Pauli paramagnetism and spin orbit scattering are significant in determining $H_{c2}(\frac{1}{2}\pi, 0)$. We note, however, that since $T^*<0$ for $r=10$, there are no regions of upward curvature of $H_{c2}(\frac{1}{2}\pi, T)$.

In Fig. 9, we have plotted $H_{c2}(\frac{1}{2}\pi, T)$ versus T/T_{c0} for $r=0.1$, for $\alpha=1$, and for various spin-orbit scattering rates. We observe that $H_{c2}(\frac{1}{2}\pi, 0)$ depends sensitively upon the spin-orbit scattering rate, and that $H_{c2}(\frac{1}{2}\pi, T)$ curves upward at T^*, which is very near to T_{c0}. For other values of α, the results are similar, except very near T_{c0}, where the slopes are different. Thus, the behavior of $H_{c2}(\frac{1}{2}\pi, 0)$ is essentially independent of α, but does depend strongly upon the effects of Pauli parmagnetism and spin-orbit scattering.

Finally, in Fig. 10, we have plotted $H_{c2}(\frac{1}{2}\pi, T)$

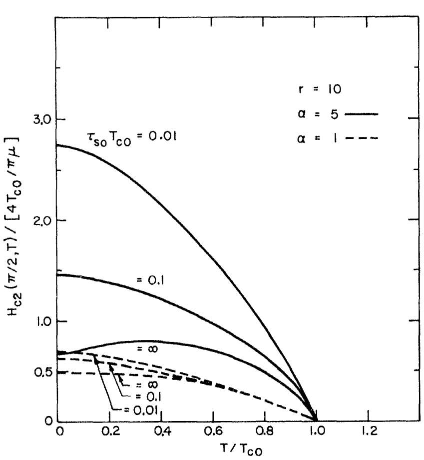

FIG. 8. Plot of $H_{c2}(\frac{1}{2}\pi, T)/H_P$ versus T/T_{c0} for $r=10$, $\alpha=1$, and 5, and for various spin-orbit scattering rates.

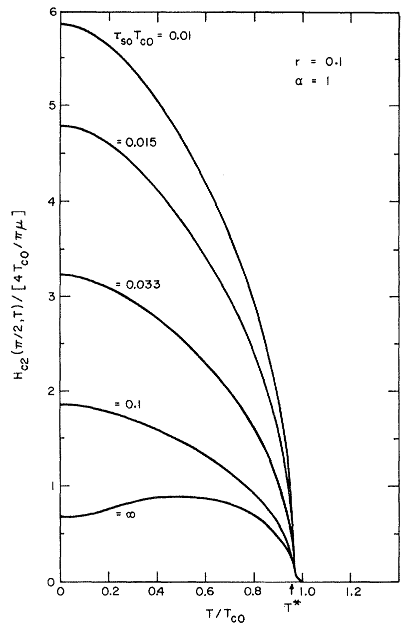

FIG. 9 Plot of $H_{c2}(\frac{1}{2}\pi, T)/H_P$ versus T/T_{c0} for $r=0.1$, $\alpha=1$, and for various spin-orbit scattering rates.

for $r=1$, for $\alpha=1$ and 5, and for various spin-orbit scattering rates. We have also indicated the curves for infinite spin-orbit scattering rate, which diverge at T^*. We observe that $H_{c2}(\frac{1}{2}\pi, 0)$ is relatively insensitive to the value of α, being determined primarily by the effects of Pauli paramag-

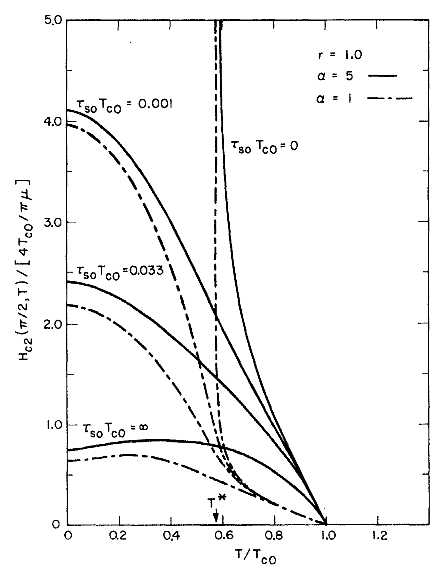

FIG 10. Plot of $H_{c2}(\frac{1}{2}\pi, T)/H_P$ versus T/T_{c0} for $r=1$, $\alpha=1$ and 5, and for various spin-orbit scattering rates. The curves for $\tau_{so}T_{c0}=0$ are equivalent to those for which the effects of Pauli paramagnetism and spin-orbit scattering have been neglected, and thus diverge at T^*.

netism and spin-orbit scattering, as was the case for $r=0.1$. However, for $T>T^*$, $H_{c2}(\frac{1}{2}\pi, T)$ depends strongly upon α and weakly upon the spin-orbit scattering rate, being similar to the curves for respectively anisotropic bulk type-II superconductors. For both $\alpha=1$ and $\alpha=5$, there is evidence of upward curvature near T^* for sufficiently strong spin-orbit rate, although for $\alpha=5$, the minimum spin-orbit scattering rate necessary for this to occur is greater than for $\alpha=1$.

We remark that Bulaevskii[25] has independently performed similar calculations of the upper critical field. He has not, however, stressed the imtance of strong spin-orbit scattering in allowing such large values of $H_{c2}(\frac{1}{2}\pi, 0)$ that seem necessary to explain experiment. At the LD theory level, $H_{c2\parallel}$ has been calculated by Boccara *et al.*,[26] who have also noted the expected upward curvature.

VIII. DISCUSSION

On the basis of the theory developed in this paper, the magnetic properties of superconducting layered compounds should be quite unusual, providing the interlayer coupling strength can be made sufficiently weak. When only orbital effects (i.e., vortices) are considered the parallel critical field, $H_{c2\parallel}$ is found to be infinite at low temperatures. We suggest physically that this result arises because the normal cores of the vortices in these materials can effectively fit inbetween the layers. This remarkable possibility suggests that layered compounds should show some equally unusual vortex dynamics and possibly Josephson-like behavior, although we have not investigated these possibilities here. As one would have guessed, the addition of Pauli paramagnetic limiting within the individual layers restores a finite $H_{c2\parallel}$, but should not alter the conclusion that in these materials the vortices are probably constrained between the layers. Also, according to our theory, as the temperature is reduced below T_c, there is a kind of "dimensional crossover" expected in which the behavior of $H_{c2\parallel}(T)$ changes from being bulklike (i.e., determined by orbital effects) to two-dimensional-like in that $H_{c2\parallel}$ is determined by the properties of the individual layers, even though long-range order is well established from layer to layer. This crossover is expected to produce a characteristic upward curvature in the temperature dependence of $H_{c2\parallel}$ providing the Pauli paramagnetic limiting is sufficiently quenched by spin-orbit scattering. Both very large critical fields and upward curvature of $H_{c2\parallel}$ have been reported for layered compounds, and it is interesting, therefore, to discuss our theoretical results in light of these experiments.

Wollman *et al.*[27] have reported a pronounced upward curvature of $H_{c2\parallel}$ in MoS_2 intercalated with Cs and Sr. Their curves can be fit by the Josephson-coupled LD model of layered compounds, as recently pointed out by Bulaevskii and Guseinov[28] on the basis of calculations similar to ours. However, in order to fit the data, they found it necessary to assume that the conducting layers in these compounds are ~100 Å apart, whereas the layer repeat distance is known to be ~10 Å. Thus, the fit is only qualitative at best and does not constitute a definitive confirmation of the theory.

Woollam *et al.* have also pointed out that a residual upward curvature of $H_{c2}(T)$ very near T_c (usually followed by a linear variation with temperature) is a common feature of the temperature dependence of H_{c2} in layered compounds. However, this residual curvature is normally present in both the parallel and perpendicular directions, and therefore not obviously due to the anisotropic (much less layered) nature of these superconductors. Moreover, in view of the broad transitions exhibited by these materials, we feel the intrinsic origin of this curvature has not been unambiguously established. The effect is ubiquitous, however, as Woollam, *et al.* have stressed.

Of the layered superconductors presently known, the best candidates for the effects predicted by our theory are the layered compounds intercalated with organic molecules (e.g., TaS_2 or $TaS_{1.6}Se_{0.4}$ intercalated with pyridine). For these materials we estimate $r<\pi/\gamma$ and therefore $T^*>0$. A systematic study of the temperature dependence of H_{c2} in these materials is presently underway.[29]

However, even without precise data on the temperature dependence of H_{c2}, it is possible to address the question as to whether the observed magnitude of $H_{c2\parallel}$ at low temperature is consistent with Pauli paramagnetic limiting. For a purely Pauli-paramagnetic-limited superconductor with strong spin-orbit scattering

$$H_{c2}(0)=(\pi T_c/3\tau_{so}\gamma\mu_B^2)^{1/2}=0.602\,(\tau_{so}T_{c0})^{-1/2}H_P\ , \quad (57)$$

where $H_P=18.4\,T_c$ kOe is the Pauli paramagnetic limiting field in the absence of spin-orbit scattering. The layered compounds in which the critical fields appear to exceed H_P most dramatically are TaS_2 and $TaS_{1.6}Se_{0.4}$ intercalated with organic molecules. Extrapolating the available data to zero temperature suggests values of $H_{c2\parallel}(0)\gtrsim 200$ kOe.[13,30] For these materials T_c is relatively low [(2–4) °K], yielding $H_P\cong 36-72$ kOe, and thus by Eq. (57), requiring spin-orbit scattering times of at least $\sim 5\times10^{-14}$ sec in order to account for the data.

We have suggested previously[7] that these very short spin-orbit scattering times might be less than the total transport scattering time τ, and therefore signal a fundamental problem in applying the standard ideas regarding Pauli paramagnetic limiting to these materials. This suggestion has led to some alternative possible interpretations.[9] However, recent low-temperature optical absorption studies by Benda *et al.*[30] on $TaS_{1.6}Se_{0.4}$, both intercalated and unintercalated, yield optical transport scattering times $\sim 4\times 10^{-15}$ sec on the basis of a simple Drude theory analysis of the data. If correct, this implies $\tau_{so}\cong 10\,\tau$, which is perhaps not unacceptable for a material containing atoms with a high atomic number such as Ta.

Thus, it seems that the very large critical field exhibited by the layered compounds is not necessarily inconsistent with the existing theory of Pauli paramagnetic limiting. It should be clearly noted, however, that this conclusion is based on accepting the very short scattering time τ found by Benda *et al.* As emphasized by those authors, this time is surprisingly short but not unacceptably so in their opinion. Final judgment must await a more complete understanding of the normal-state transport properties of these materials, including perhaps the effects of the recently discovered charge-density waves.[31]

In conclusion, it is clear that the superconducting properties of layered compounds continue to be of considerable interest both theoretically and experimentally. Indeed, as we have seen from the simple theory presented here, these superconductors seem quite likely to exhibit some rather novel type-II superconducting behavior. At the same time many interesting theoretical questions remain to be studied, in particular, the nature of the vortex dynamics expected in such layered or periodic systems and its relation to true Josephson behavior.

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APPENDIX

We wish to solve the integral equation for the product of two Green's functions given in the text. To do so, we define

$$S_\omega(\vec{p},p_z)=\frac{2\pi T}{N(0)}\int\frac{d^2p'}{(2\pi)^2}\int_{-\pi/s}^{\pi/s}\frac{dp_z'}{2\pi}\,\langle G^n_{\omega\sigma}(\vec{p}\,',p_z')G^n_{-\omega,-\sigma}(\vec{p}-\vec{p}\,',p_z-p_z')\rangle\,, \tag{A1}$$

and $S^0_\omega(\vec{p},p_z)$ is obtained from $S_\omega(\vec{p},p_z)$ by averaging the two Green's functions over the impurity sites independently. The integral equation corresponding to Fig. 3 is found to be

$$S_\omega(\vec{p},p_z)=S^0_\omega(\vec{p},p_z)\left(1+ns\int\frac{d^2p'}{(2\pi)^2}\int_{-\pi/s}^{\pi/s}\frac{dp_z'}{2\pi}[(V_1+iV_{so}(\hat{p}\times\hat{p}')\cdot\vec{\sigma})\,S_\omega(\vec{p}\,',p_z')(V_1-iV_{so}(\hat{p}\times\hat{p}')\cdot\vec{\sigma})]\right), \tag{A2}$$

where $\hat{p}$ is a unit vector parallel to the layers. To solve this integral equation, we proceed analogously to WHH,[20] and obtain

$$S_\omega(\vec{p},p_z)=S^0_\omega(\vec{p},p_z)\left(1+\frac{1}{2\pi T}\int d\hat{p}'\{\tau^{-1}S^{(1)}_\omega(\hat{p}')+[\tau_1^{-1}-\tfrac{2}{3}\tau_{so}^{-1}(\hat{p}\cdot\hat{H})^2]S^{(2)}_\omega(\hat{p}')\vec{\sigma}\cdot\vec{H}\,\mathrm{sgn}\,\omega\}\right), \tag{A3}$$

where we have written

$$S_\omega(\vec{p},p_z)=S^{(1)}_\omega(\hat{p})+S^{(2)}_\omega(\hat{p})\vec{\sigma}\cdot\vec{H}\,\mathrm{sgn}\,\omega. \tag{A4}$$

In Eq. (A3), the factor $\frac{2}{3}$ arises from the fact that the electron spins are not restricted to the directions parallel to the layers, whereas the momenta of the electrons are restricted to those directions during the scattering process. Solving for S, we then use Eq. (30) to obtain Eq. (32), the implicit relation for H_{c2}.[21]

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