

⁴G. A. Alers, Phys. Rev. **119**, 1532 (1960).

⁵J. Ferreira da Silva, J. Scheffer, N. W. J. van

Duykeren, and Z. Dokoupil, Phys. Letters **12**, 166 (1964).

TEMPERATURE AND PURITY DEPENDENCE OF THE SUPERCONDUCTING CRITICAL FIELD, H_{C2}

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A solution is given for the temperature and mean-free-path dependence of the upper critical field, H_{C2} , of a bulk, type-II superconductor. Spin paramagnetic effects are omitted here.

Previously, this calculation has been carried out in several limiting cases. The Ginzburg-Landau-Abrikosov-Gor'kov¹⁻³ (GLAG) theory, although applicable for all mean free paths, l , is restricted to temperatures, T , in the immediate vicinity of the zero-field transition temperature, T_c . Recently, Maki⁴ and de Gennes⁵ have independently solved for the full temperature dependence of H_{C2} in the dirty, or small- l , limit. In addition, Gor'kov⁶ has determined the value of H_{C2} at zero temperature for clean ($l \rightarrow \infty$) samples.

We are concerned exclusively with the critical field at a second-order transition, where the superconductor gap function, $\nabla(\vec{r})$, is vanishing. Thus the analysis may be based upon a determination of the largest field for which the linear, homogeneous equation for $\nabla(\vec{r})$, due to Gor'kov,³ has a nonzero, bounded solution. This equation may be written in the form

$$\chi^{\text{op}} \Delta(\vec{r}) = \ln(T_c/T) \Delta(\vec{r}), \quad (1)$$

where

$$\chi^{\text{op}} \Delta(\vec{r}) \equiv \int d^3r' X(\vec{r}, \vec{r}') \Delta(\vec{r}'), \quad (2)$$

and

$$X(\vec{r}, \vec{r}') \equiv \sum_{\nu=-\infty}^{\infty} \left[|2\nu+1|^{-1} \delta(\vec{r}-\vec{r}') - \frac{T}{N(0)} \langle G_{\omega H}(\vec{r}, \vec{r}') G_{-\omega H}(\vec{r}, \vec{r}') \rangle \right]. \quad (3)$$

Here $\omega = \pi T(2\nu+1)$, $N(0)$ is the density of states

at the Fermi surface, and we measure temperatures and frequencies in energy units. $G_{\omega H}$ is the one-electron Green's function in the presence of both a uniform, static magnetic field, \vec{H} , and a particular fixed configuration of impurities. The angular brackets in Eq. (3) indicate an averaging over a random ensemble of impurity distributions.

In the field-free case, Abrikosov and Gor'kov^{7,3} have discussed the impurity-averaging procedure. They show that to lowest order in the impurity concentration, a physically valid limit, one need only take account of unlinked chains and ladders in a diagrammatic development. In the presence of the magnetic field, their procedure need be modified only by allowing the field to affect electron propagation between independent impurity-scattering events, but not during a scattering event, which is of very short range.

For actual experiments, it is almost always true that the spacing of the Landau levels in the field is small compared to their thermal and impurity broadening. In this semiclassical limit, the magnetic field enters the expression for the Green's function merely via a phase factor.

In this manner it is found that the operator of Eq. (2) may be written

$$\chi^{\text{op}} = \sum_{\nu=-\infty}^{\infty} \chi_{\omega H}^{\text{op}}, \quad (4)$$

$$\chi_{\omega H}^{\text{op}} = |2\nu+1|^{-1} - \frac{s_{\omega H}^{\text{op}}}{[1 - (s_{\omega H}^{\text{op}}/2\pi T\tau)]}, \quad (5)$$

where $\tau = l/v_f$, and $s_{\omega H}^{\text{op}}$ is an integral operator with eigenvalue equation

$$s_{\omega H}^{\text{op}} \varphi(\vec{r}) \equiv \frac{T}{N(0)} \int d^3r' \langle G_{\omega H}(\vec{r}, \vec{r}') \rangle \langle G_{-\omega H}(\vec{r}, \vec{r}') \rangle \varphi(\vec{r}') \quad (6)$$

$$s_{\omega H}^{\text{op}} \varphi(\vec{r}) = s_{\omega H} \varphi(\vec{r}). \quad (7)$$

$\langle G_{\omega H} \rangle$ is the impurity-averaged, single-particle Green's function,

$$\langle G_{\omega H}(\vec{r}, \vec{r}') \rangle = -\frac{m}{2\pi|\vec{r}-\vec{r}'|} \exp\left\{ \frac{ie}{c} \vec{A}\left(\frac{\vec{r}+\vec{r}'}{2}\right) \cdot (\vec{r}-\vec{r}') + \left[i\frac{\omega}{|\omega|} p_f - \frac{|\omega|}{v_f} - \frac{1}{2l} \right] |\vec{r}-\vec{r}'| \right\}. \quad (8)$$

Equation (7) can be cast into the gauge-invariant form

$$\frac{T}{2\nu} \int d^3\rho \frac{1}{\rho^2} \exp\left\{ -\left(\frac{2|\omega|}{v_f} + \frac{1}{l} \right) \rho \right\} \exp\{ -i\vec{\rho} \cdot [i\nabla + (2e/c)\vec{A}(\vec{r})] \} \varphi(\vec{r}) = s_{\omega H} \varphi(\vec{r}). \quad (9)$$

Due to the isotropy of the $\vec{\rho}$ integration, $s_{\omega H}^{\text{OP}}$ can only be a function of scalar operators.

The only two such independent operators which can be constructed are

$$\mathfrak{D}_1 \equiv [i\nabla + 2(e/c)\vec{A}(\vec{r})]^2,$$

and

$$\mathfrak{D}_2 \equiv \vec{H} \cdot [i\nabla + 2(e/c)\vec{A}(\vec{r})]. \quad (10)$$

Hence, the eigenfunctions, $\varphi(\vec{r})$, of $s_{\omega H}^{\text{OP}}$ are independent of ω ; and the processes of solving the eigenvalue problem, Eq. (9), and summing over ν , Eqs. (4) and (5), may be reversed.

To obtain the largest field for which a solution of Eq. (1) exists, the only eigenvalue problem which need be considered is identical with that encountered in the GLAG theory; namely, the simultaneous ground state of the commuting operators \mathfrak{D}_1 and \mathfrak{D}_2 . Following Abrikosov,² the solutions are

$$\varphi(\vec{r}) \propto \exp\{ (2eH/c)[ix_0y - \frac{1}{2}(x-x_0)^2] \}, \quad (11)$$

degenerate with respect to an arbitrary x_0 . The corresponding eigenvalue of $s_{\omega H}^{\text{OP}}$ is

$$s_{\omega H} = \int d^3r \varphi^* s_{\omega H}^{\text{OP}} \varphi / \int d^3r |\varphi|^2 = 2\pi T (2|\omega| + \tau^{-1})^{-1} I(\alpha), \quad (12)$$

where

$$\alpha \equiv \frac{(2eHv_F^2/c)^{1/2}}{(2|\omega| + \tau^{-1})}, \quad (13)$$

$$I(\alpha) \equiv (2/\alpha) \int_0^\infty \exp(-w^2) \arctan \alpha w dw. \quad (14)$$

Finally, the desired critical field H_{c2} is given implicitly as a solution of

$$\ln\left(\frac{T_c}{T}\right) = \sum_{\nu=-\infty}^{\infty} \left\{ |2\nu+1|^{-1} - \frac{s_{\omega H}}{1 - (s_{\omega H}/2\pi T\tau)} \right\}. \quad (15)$$

Note that expansions of $I(\alpha)$ in powers of α , which yields the $T \rightarrow T_c$ limit of the GLAG theory,¹⁻³ and also the dirty limit (small τ),^{4,5}

are asymptotic, rather than convergent, series.

Numerical solutions of Eqs. (12)-(15) are plotted in Fig. 1 as a function of reduced temperature, t , for various degrees of purity as given by the reduced collision frequency,

$$\lambda = (2\pi T_c \tau)^{-1} = 0.882 \xi_0 / l. \quad (16)$$

The magnetic field units are reduced in such a way that the plot is of an effective Ginzburg-Landau parameter,²

$$\kappa_1(T, \lambda) \equiv H_{c2}(T, \lambda) / \sqrt{2} H_c(T), \quad (17)$$

where $H_c(T)$ is the thermodynamic critical field. The usual Ginzburg-Landau parameter, κ , is obtained as $\kappa = \kappa_1(T_c, \lambda)$.

A more detailed derivation of Eqs. (12)-(15), together with a comparison of our results with the large amount of experimental data now available, will be submitted for publication elsewhere.

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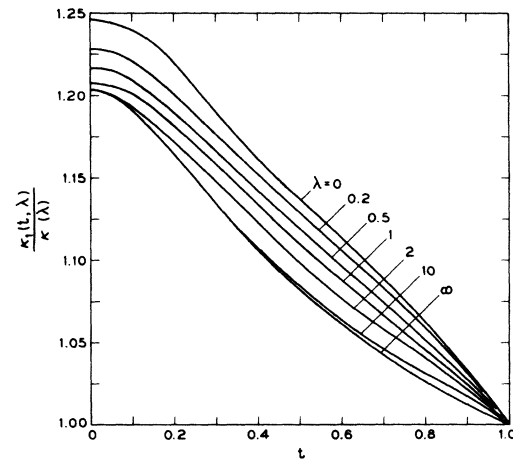


FIG. 1. The effective Ginzburg-Landau parameter, reduced by its value at T_c , as a function of reduced temperature, for various degrees of purity.

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¹V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. 20, 1064 (1950).

²A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. 32, 1442 (1957) [translation: Soviet Phys.-JETP 5, 1174 (1957)].

³L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 36, 1918 (1959) [translation: Soviet Phys.-JETP 9,

1364 (1959)]; Zh. Eksperim. i Teor. Fiz. 37, 1407 (1959) [translation: Soviet Phys.-JETP 10, 998 (1960)].

⁴K. Maki, Physics 1, 21 (1964).

⁵P. G. de Gennes, to be published.

⁶L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 37, 833 (1959) [translation: Soviet Phys.-JETP 10, 593 (1960)].

⁷A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 35, 1558 (1958) [translation: Soviet Phys.-JETP 8, 1090 (1959)].

MAGNETIC, ELECTRIC, AND CRYSTALLOGRAPHIC PROPERTIES OF GALLIUM IRON OXIDE

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Gallium iron oxide, $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$ with $0.7 \leq x \leq 1.4$, was first prepared by Remeika and shown to be ferromagnetic and piezoelectric.¹ This is the only crystal known to possess both properties. Recently, Rado² has observed a magnetoelectric effect in $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$. He showed this effect to be larger by an order of magnitude than that in any previously measured material, and also that the induced polarization is normal to the applied field. On the basis of a complete determination³ of the crystal structure and of new magnetization measurements, we propose a magnetic-structure model that clarifies the results of previous studies.^{2,4,5} We also suggest that the piezoelectricity originates in the oxygen-atom arrangement, in contrast to the ferromagnetism which is primarily due to the cations.

The unit cell and space group of $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$ have been reported by Wood.⁶ The space group is $C_{2v}^9\text{-}Pc2_1n$, with eight formula weights per unit cell. The arrangement of cations is shown in Fig. 1, the oxygens being omitted from the figure for clarity. Each of the four cations in the asymmetric unit (e.g., within the area bounded by $a/4$ and b), at site positions with point symmetry C_1-1 , are related to three other equivalent cations in the unit cell by the space-group symmetry. The ferromagnetic axis is c , and the polar axis is b (i.e., $\perp c$). If we assume no integral change in cell size and no loss of symmetry between the chemical and magnetic cells, the most probable Shubnikov groups for the magnetic unit cell are then $Pc2_1n$, $Pc2_1'n'$, $Pc'2_1n'$, and $Pc'2_1'n$. The first of these is antiferromagnetic; the other three are ferromagnetic, with a spontaneous mo-

ment allowed along the a , b , and c axes, respectively. Hence, the most likely Shubnikov group is $Pc'2_1'n$. Rado² has independently arrived at the similar conclusion that the magnetic point group is $2'm'm$. This should be written $m'2'm$ in terms of Wood's assignment⁶ of axes, which we have retained. The magnetic space group $Pc'2_1'n$ requires the spin components in the ab plane to be antiparallel, with all the c -axis components parallel (for a given set of symmetry-related sites).

The magnetic moment per ferric ion, for stoichiometric GaFeO_3 , is reported⁵ to be $0.76 \mu_B$. Assuming an S-state ion, with the spin at Fe(1) making an angle θ_1 , and that at Fe(2) an angle θ_2 with the c axis, then

$$\frac{5}{2}(\cos\theta_1 + \cos\theta_2) = 0.76.$$

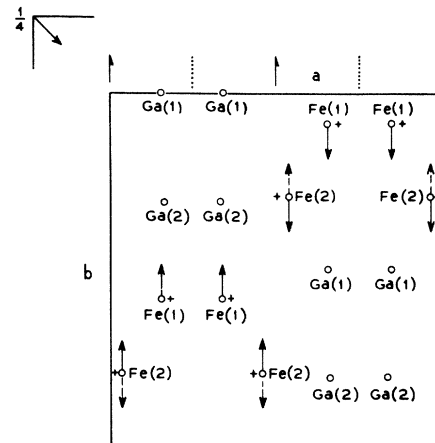


FIG. 1. Schematic arrangement of cations and magnetic spins in $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$. Spin components in the ab plane are represented by arrows, along c by plus signs.