nected with sample structure can be avoided by careful preparation and encapsulation techniques described elsewhere.[8]

The assembled data are consistent with changes in K of 5.5% from room temperature to the melting point and a further 5.0% at the melting transition. These compare favorably with the values (5.0 ± 1.5) and (5.1 ± 0.3)% we reported previously (the latter value was obtained as the mean of repeated measurements). The absolute Knight shift at room temperature in Fig. 1 agrees with accepted values for Cu,[9] of which the higher (~ 0.236) are probably the more reliable, owing to skin-effect shifts.

We note further that the relaxation rates measured by EZ confirm the motional narrowing observed by Flynn and Seymour[5] (FS), and allow an estimate to be made of the activation energy Q for self-diffusion. The result, $Q = 2.04 \pm 0.02$ eV, appeared to be in better agreement with existing radio-tracer studies than the value of $Q = 2.08_5 \pm 0.04$ eV obtained by FS from absolute diffusion rates and an estimated D_0 (the diffusion rates of EZ and FS agree where they overlap). Results derived from direct observation of T_2 should indeed be the more precise. Unfortunately, recent more accurate tracer studies[10] give $Q = 2.19 \pm 0.01$ eV. This tends to confirm the impression that nuclear-magnetic-resonance (NMR) methods (except perhaps those using temperature ranges extended by the Ailion-Slichter[11] or related methods) do not compare in accuracy or reliability with alternative radio-tracer techniques when suitable isotopes are available.

Note added in manuscript. We have been notified through a publication of the Israel Atomic Energy Commission that further investigations by EZ confirm our belief that their published Knight-shift data contain substantial systematic errors. It appears that the anomaly at ~ 1000 °K is indeed an experimental artifact. The 7% discrepancy between their NMR results and the tracer values of the activation energy for self-diffusion in copper has not, as yet, been explained.

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[1]R. L. Odle and C. P. Flynn, J. Phys. Chem. Solids 26, 1685 (1965).
[2]W. W. Warren and W. G. Clark, Phys. Rev. 177, 600 (1969).
[3]W. W. Warren and W. G. Clark, Phys. Rev. B 1, 24 (1970).
[4]U. El-Hanany and D. Zamir, Phys. Rev. 183, 809 (1969).
[5]C. P. Flynn and E. F. W. Seymour, Proc. Phys. Soc. (London) 77, 922 (1961).
[6]A. C. Chapman, P. Rhodes, and E. F. W. Seymour, Proc. Phys. Soc. (London) B70, 345 (1957).
[7]J. Bensel and J. A. Gardner, J. Appl. Phys. 41, 1157 (1970).
[8]J. A. Gardner and C. P. Flynn, Phil. Mag. 15, 1233 (1967).
[9]W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. 2; H. S. Gutowski and B. R. McGarvey, J. Chem. Phys. 20, 1472 (1952).
[10]S. J. Rothman and N. L. Peterson, Phys. Status Solidi 35, 305 (1969).
[11]D. Ailion and C. P. Slichter, Phys. Rev. 135, A109 (1964).

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Healing Length of the Superconducting Order Parameter*

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We calculate the healing length of the superconducting order parameter near $T = T_c$ by means of a variational method based on the Neumann-Tewordt expression for the free energy of an inhomogeneous superconductor. The result for the correction to the Ginzburg-Landau healing length near $T = T_c$ indicates that the healing takes place over distances of the order of the coherence length at all temperatures, in disagreement with a recent calculation which predicts healing over atomic distances at low temperatures.

I. INTRODUCTION

The problem of a superconductor in contact with a magnetic material is one of current interest. Because of the large pair breaking, the superconducting order parameter $\Delta(\vec{r})$ is assumed to vanish in the magnetic material; the boundary condition on $\Delta(\vec{r})$ in the superconductor is taken to be $\Delta(\vec{r}) = 0$ at the interface. To obtain qualitative predictions for the properties of this system, one can take $\Delta(\vec{r})$ to jump at the interface to the value (Δ_∞) characteristic of wholly superconducting material at the temperature T. If, however, it is desired to push the model somewhat further, one is required to determine at least approximately how $\Delta(\vec{r})$ heals on going into the superconductor.

The position dependence of $\Delta(\vec{r})$ in the superconductor is known exactly at $T=T_c$ since an analytic solution of the Ginzburg-Landau equation is possible: If the plane of contact is the plane $x=0$, the solution for a superconductor of infinite thickness is

$$\Delta(x) = \Delta_\infty \tanh(x/\sqrt{2}\,\xi_{\mathrm{GL}}) \quad , \tag{1}$$

where ξ_{GL} is the Ginzburg-Landau coherence length. No exact solutions are known at lower temperatures, however, and it is necessary to resort to approximations.

Recently, Bardeen *et al.*[1] (BKJT) have presented a theory of inhomogeneous pure superconductors based on WKBJ solutions of the Bogoliubov equations, and a variational method based on this theory has been used[2] to estimate the position dependence of $\Delta(x)$ for all temperatures less than T_c: The method was to assume that the form $[\xi=\hbar v_F/\pi\Delta_\infty(T)]$

$$\Delta(x) = \Delta_\infty \tanh(dx/\xi) \tag{2}$$

was a good approximation at all temperatures; the adjustable parameter d was determined by minimizing the BKJT free-energy expression. It was found that d extrapolated, as it should, to the correct value at $T=T_c$. The result of greatest interest in this calculation was the strong temperature dependence of d; d extrapolated to a very large value at low temperatures, and it was concluded in Ref. 2 that the order parameter heals over atomic distances.

The above result is surprising in view of the weak temperature dependence found for other quantities in the theory of inhomogeneous superconductors; the ratio $H_{c2}(T)/H_c(T)$, for example, changes by only 20% or so from $T=0\,^\circ$K to $T=T_c$.[3] As a check on the calculation of Ref. 2, we have calculated the first-order correction in $1-T/T_c$ to the Ginzburg-Landau result for the healing length using the theory of Neumann and Tewordt[4] for the free energy of an inhomogeneous superconductor near $T=T_c$. In Sec. II we derive the Neumann-Tewordt free-energy expression from the BKJT formalism, and in Sec. III the temperature dependence of the healing length near $T=T_c$ is obtained variationally. We find that the correction to the Ginzburg-Landau result is only one-fiftieth as large as the result of Ref. 2, and we conclude there is no evidence that the order parameter heals over atomic distances at low temperatures.

II. DERIVATION OF THE NEUMANN-TEWORDT FREE ENERGY

The result of Bardeen *et al.*[1] for the free energy of an inhomogeneous pure superconductor [relative to the state with $\Delta(\vec{r})\equiv\Delta_\infty$] is, for the geometry under consideration,

$$\Delta G = \Delta G_b + V^{-1}\int dx\,(\delta^2-1)\,\Delta_\infty^2 + (\Delta_\infty/2\pi^2)\int_0^{k_F} k\,dk \int_1^\infty d\Lambda\,\Sigma(k,\Lambda)\tanh(\tfrac{1}{2}\beta\Delta_\infty\Lambda), \tag{3}$$

where $\delta=\Delta(x)/\Delta_\infty$, ΔG_b is the contribution from the bound states, $\Lambda=E/\Delta_\infty$, and Σ is the sum of the phase shifts for the scattering states. Equation (3) can be rewritten as

$$\Delta G = \Delta G_b + (\Delta_\infty/2\pi^2)\int_0^{k_F} k\,dk \int^\infty d\Lambda \tanh(\tfrac{1}{2}\beta\Delta_\infty\Lambda) \times[\Sigma+\tfrac{1}{2}\int_0^\infty d\zeta\,(\delta^2-1)(\Lambda^2-1)^{-1/2}]\,, \tag{4}$$

where $\zeta=(2m\Delta_\infty/\hbar^2 k)x$.

In a previous publication,[5] the author has derived the Neumann-Tewordt free-energy expression for the isolated vortex geometry from the BKJT theory; the demonstration for the geometry under consideration here is very similar and we give only the main points.

The result for Σ obtained in Ref. 5 is easily converted to the new geometry; we find

$$\Sigma = -\tfrac{1}{2}\int_0^\infty d\zeta\,\{\Lambda^{-1}(\delta^2-1)+\Lambda^{-3}[\tfrac{1}{4}(\delta^4-1)+(\delta')^2] + \Lambda^{-5}[\tfrac{5}{2}(\delta\delta')^2+\tfrac{1}{8}(\delta^6-1)-2\delta'\delta'''-(\delta'')^2]\} \tag{5}$$

and

$$\Sigma+\tfrac{1}{2}\int_0^\infty d\zeta\,(\delta^2-1)(\Lambda^2-1)^{-1/2} = \tfrac{1}{2}\int_0^\infty d\zeta\,\{-\Lambda^{-3}[\tfrac{1}{4}(1-\delta^2)^2+(\delta')^2] + \Lambda^{-5}[-\tfrac{5}{2}(\delta\delta')^2+\tfrac{1}{8}(-\delta^6+3\delta^2-2)+2\delta'\delta'''+(\delta'')^2]\}\,. \tag{6}$$

In Eqs. (5) and (6), the prime denotes differentiation with respect to ζ. We now go over to the variable x and introduce the temperature-dependent coherence length ξ by

$$\xi(T) = \hbar v_F/\pi\Delta_\infty(T)\ . \tag{7}$$

On substituting the result (6) into Eq. (4) and performing the k and Λ integrals as in Ref. 5, we find

$$\Delta G = \Delta G_b + \Delta G_o + \left(\frac{\Delta_\infty k_F^2}{2\pi^3 \xi}\right)\int_0^\infty dx \left[\frac{7\zeta(3)}{4\pi^2}\left(\frac{\Delta_\infty}{2T}\right)^2 \left((1-\delta^2)^2 + \frac{1}{3}\pi^2\xi^2(\delta')^2\right) + \frac{31\zeta(5)}{\pi^4}\left(\frac{\Delta_\infty}{2T}\right)^4 \left(\frac{-5\pi^2\xi^2}{24}(\delta\delta')^2 + \frac{1}{8}(-\delta^6 + 3\delta^2 - 2) + \frac{\pi^4\xi^4}{80}\left[2\delta'\delta''' + (\delta'')^2\right]\right)\right], \quad (8)$$

where the derivatives are now with respect to x, and ΔG_o represents terms of odd order in $\Delta_\infty/2T$ arising from the Λ integration. Equation (8) can be rewritten using the expansions of $\Delta_\infty/2T$ and H_c given in Ref. 5; after an integration by parts, the result is

$$\Delta G = \Delta G_b + \Delta G_o + \left(\frac{H_c^2}{4\pi}\right)\int_0^\infty dx\left[\tfrac{1}{6}\pi^2\xi^2(\delta')^2 + \tfrac{1}{2}(1-\delta^2)^2\right] + \frac{H_c^2}{4\pi}\,\frac{31\zeta(5)\,(1-t)\,\pi^4\xi^4}{490\,\zeta^2(3)}\,\delta'\delta''\Big|_{x=0}^{\infty} + \frac{H_c^2}{4\pi}\,\frac{31\zeta(5)\,(1-t)}{98\,\zeta^2(3)}\int_0^\infty dx\left[-\delta^2(1-\delta^2)^2 + \tfrac{2}{3}\pi^2\xi^2(\delta')^2 - \tfrac{5}{3}\pi^2\xi^2(\delta\delta')^2 - \tfrac{1}{10}\pi^4\xi^4(\delta'')^2\right], \quad (9)$$

where $t = T/T_c$. The term arising from the integration by parts vanishes for any analytic function of x antisymmetric about $x = 0$, such as the variational function of Eq. (2). The terms ΔG_b and ΔG_o are of odd order in $(1 - T/T_c)^{1/2}$ and we neglect them. The remainder of the right-hand side of Eq. (9) is identical to the Neumann-Tewordt expression for the free energy of an inhomogeneous pure superconductor in this geometry.

III. HEALING LENGTH NEAR $T = T_c$

The Neumann-Tewordt[4] expression for the free energy of an inhomogeneous superconductor in zero magnetic field, relative to the state with $\Delta(\vec{r}) \equiv \Delta_\infty$, is

$$\Delta G = (H_c^2/4\pi)\int_0^\infty dx\,\{[\tfrac{1}{2}(1-\delta^2)^2 + \lambda^2\kappa_3^{-2}(\delta')^2] + (1-t)[\eta_c\delta^2(1-\delta^2)^2 - \eta_k\lambda^2\kappa_3^{-2}(1-\delta^2)(\delta')^2 + \eta_w\lambda^2\kappa_3^{-2}(\delta\delta')^2 + (\eta_{4d} + 3\eta_{4c})\lambda^4\kappa_3^{-4}(\delta'')^2]\}, \quad (10)$$

where η_c, η_k, η_w, η_{4d}, and η_{4c} are constants given by Eqs. (2) and (3) of Neumann and Tewordt[4]; $\eta_c = -31\zeta(5)/98\zeta^2(3)$ is independent of the mean free path l, but the other quantities depend on $\alpha = \pi\xi(0)/2\gamma l = 0.882\xi(0)/l$. λ is the weak-field local penetration depth, defined (in the usual notation) by

$$\frac{1}{\lambda^2} = \frac{2}{\lambda_L^2(0)}(\Delta\beta)^2 \sum_{n=0}^{\infty}\frac{\pi}{[(\omega\beta)^2 + (\Delta\beta)^2]^{3/2}} \times\left(1 + \frac{1}{2\tau}\,\frac{1}{(\omega^2+\Delta^2)^{1/2}}\right)^{-1}. \quad (11)$$

Equation (10) is valid for both pure and impure superconductors; the first square brackets contain the Ginzburg-Landau term and the second the first-order correction in $1 - T/T_c$.

To determine the healing length, we use the variational function of Ref. 2,

$$\delta = \tanh(dx/\xi), \quad (12)$$

in Eq. (10); the result is

$$\Delta G = (H_c^2/4\pi)\tfrac{2}{3}\{[\tfrac{1}{2}(\xi/d) + (d\lambda^2/\kappa_3^2\xi)] + (1-t)\tfrac{1}{5}[(\eta_c\xi/d) + (\eta_w - 4\eta_k)(d\lambda^2/\kappa_3^2\xi) + (\eta_{4d} + 3\eta_{4c})(4d^3\lambda^4/\kappa_3^4\xi^3)]\}. \quad (13)$$

The required expansion of the quantity λ^2/κ_3^2 in powers of $(1-t)$ can be obtained from Eq. (11) and[4] $\kappa_3 = \kappa[1 + (1-t)\phi]$, where ϕ is defined by Eq. (8) of Neumann and Tewordt.[4] The result is

$$\lambda^2/\kappa_3^2 = \tfrac{1}{6}\pi^2\xi^2[8S_{21}/7\zeta(3)][1 - (1-t)(1 + \phi + 2\eta_c)], \quad (14)$$

where

$$S_{21} = \sum_{n=0}^{\infty}(2n+1)^{-2}(2n+1+\alpha)^{-1}. \quad (15)$$

Note that

$$\lim(\xi^2/\xi_{\rm GL}^2) = 6/\pi^2 \text{ as } T \to T_c. \quad (16)$$

On minimizing ΔG with respect to d and expanding d as

$$d = d_0 + (1-t)d_1, \quad (17)$$

one finds

$$d_0 = \left(\frac{6}{\pi^2}\right)^{1/2}\left(\frac{7\zeta(3)}{8S_{21}}\right)^{1/2}\frac{1}{\sqrt{2}} \quad (18)$$

and

$$d_1 = d_0[\tfrac{1}{2} + \tfrac{1}{2}\phi + \tfrac{6}{5}\eta_c + \tfrac{1}{5}(-\tfrac{1}{2}\eta_w + 2\eta_k - 3\eta_{4d} - 9\eta_{4c})]. \quad (19)$$

For a pure superconductor, $\eta_k = 6\eta_c$, $\eta_w = 4\eta_c$, $\eta_{4d} = 0$, $\eta_{4c} = \frac{6}{5}\eta_c$, and $\phi = -1 - 4\eta_c$; Eq. (19) then reads

$$d_1 = 0.218 d_0 \quad (20)$$

or

$$d = d_0[1 + 0.218(1-t)]. \quad (21)$$

Since the correction term to the Ginzburg-Landau result is so small, there is no evidence that the healing length is much different from ξ at any temperature.

On the other hand, the result for d obtained in Ref. 2 is

$$d \approx d_0[1+10(1-t)] \qquad (22)$$

near $T = T_c$; the two results differ by a factor of 50 in the correction to the Ginzburg-Landau result. The source of the discrepancy is at present unknown and further work is required. It is clear, however, 'hat Eq. (21), rather than Eq. (22), is the correct result for the healing length in "this model."

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[1]J. Bardeen, R. Kümmel, A. E. Jacobs, and L. Tewordt, Phys. Rev. 187, 556 (1969).

[2]R. M. Cleary, Phys. Rev. B 2, 3577 (1970).

[3]E. Helfand and N. R. Werthamer, Phys. Rev. 147, 288 (1966).

[4]L. Neumann and L. Tewordt, Z. Physik 189, 55 (1966).

[5]A. E. Jacobs, Phys. Rev. B 2, 3587 (1970).

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Spin-Hamiltonian Parameters and Spin-Orbit Coupling for V^{3+} in ZnO†

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The spin-Hamiltonian parameters for ZnO : V^{3+} have been refined using electron-paramagnetic-resonance (EPR) line position calculations. The principal sources of error are discussed. The accurate spin-Hamiltonian parameters are used to discuss the spin-orbit coupling within the 3d manifold of electronic states.

Values for the spin-Hamiltonian parameters of V^{3+} in ZnO have been reported recently by Filipovich, Taylor, and Coffman[1] and by Hausmann and Blaschke.[2] Significant differences between several of the reported parameter values, and the question of the importance and magnitude of the anisotropy of the spin-orbit coupling coefficients, have prompted us to reinvestigate these parameter values using an accurate EPR spectrum calculation. The experimental data were fitted with an axial-symmetry spin Hamiltonian which included the nuclear Zeeman and electric quadrupole interactions:

$$\mathcal{H} = D(S_z^2 - \tfrac{2}{3}) + g_{\parallel}\mu_B H_z S_z + g_{\perp}\mu_B (H_x S_x + H_y S_y) + A S_z I_z + B(S_x I_x + S_y I_y) + g_n \mu_N \vec{H}\cdot\vec{I} + Q'(I_z^2 - \tfrac{21}{4}). \qquad (1)$$

The (isotropic) nuclear g value for V^{51} was taken from the Varian NMR tables.[3] The resonance field values and intensities were calculated using the program MAGSPEC,[4] which determined the resonance fields for a given set of parameter values in (1) to within at least ± 0.1-G accuracy (see Table I), and correctly determines the intensities by computing the transition probabilities from the radiation Hamiltonian and the matrix of the eigenvectors of $\mathcal{H}$. The results were compared with the accurate field and frequency measurements of Coffman and Filipovich.[5] Parameter variation after each calculation, so as to decrease the errors $(H^i_{expt} - H^i_{calc})$ for all i absorption lines, was done by inspection using previously derived perturbation theory formulas.

The spectrum matching procedure was carried out for two EPR bands: one measured with $\vec{H}_0 \parallel c$, $\nu = 9.30875$ GHz with center at about 4800 G, and the other with $\vec{H}_0 \perp c$, $\nu = 9.51026$ GHz and center at about 6400 G. The value for $g_{\parallel}$ was assumed from the previous study,[1] since it can be measured independently of all other parameters. The values of D, A, $g_{\perp}$, B, and Q' were varied until one set of values gave the best agreement with experiment in a least-squares sense with respect to the measured line centers. The values of the parameters so derived (see Table I) led to the calculated line positions which are compared with experiment in

TABLE I. Spin-Hamiltonian parameters for ZnO:V^{3+} with estimated probable errors.

Parameter	Value	Estimated error
D/hc	± 0.74637 cm^{-1}	± 0.0005 cm^{-1}
$g_{\parallel}$	1.9451	± 0.0005
$g_{\perp}$	1.9329	± 0.0005
A/hc	$\pm 66.0\times 10^{-4}$ cm^{-1}	$\pm 0.5\times 10^{-4}$ cm^{-1}
B/hc	$\pm 77.1\times 10^{-4}$ cm^{-1}	$\pm 0.5\times 10^{-4}$ cm^{-1}
Q'/hc	0.0 cm^{-1}	± 0.00005 cm^{-1}