Anisotropic s-wave superconductivity in CaAlSi single crystals from penetration depth measurements

Ruslan Prozorov
Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA

Tyson A. Olleheiser and Russell W. Giannetta
Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801, USA

Kentaro Uozato and Tsuyoshi Tamegai
Department of Applied Physics, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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In- and out-of-plane London penetration depths were measured in CaAlSi single crystals ($T_c = 6.2$ and 7.3 K) using a tunnel-diode resonator. A full three-dimensional (3D) BCS analysis of the superfluid density is consistent with a prolate spheroidal gap, with a weak-coupling BCS value in the $ab$ plane and stronger coupling along the $c$ axis. The gap anisotropy was found to significantly decrease for higher $T_c$ samples.

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Superconductors with an AlB$_2$ structure have received increased attention after the discovery of superconductivity at 39 K and especially after identification of two distinct gaps in MgB$_2$.\textsuperscript{1-3} It is believed that two gaps survive because of reduced interband scattering due to the different dimensionality of two-dimensional (2D) $\sigma$ and three-dimensional (3D) $\pi$ bands. Investigating materials with similar crystal and band structure is therefore important for understanding the mechanism of superconductivity in this class of hexagonal-layer compounds. In this paper we study CaAlSi which has been synthesized long ago,\textsuperscript{4} but in which superconductivity was discovered only recently.\textsuperscript{5} Band structure calculations show highly hybridized three-dimensional interlayer and $\pi^*$ bands.\textsuperscript{6,7} Although most studies of CaAlSi indicate s-wave pairing, deviations from a single isotropic gap behavior have been reported.\textsuperscript{5,8–11} Magnetic measurements indicate a full developed s-wave BCS gap.\textsuperscript{9,12} Angle-resolved photoemission spectroscopy\textsuperscript{10} revealed the same gap magnitude on the two bands with a moderately strong coupling value for the reduced gap $2\Delta/k_BT_c$ = 4.2. Together with specific heat measurements\textsuperscript{11} it provided reliable evidence for a three-dimensional moderately strong-coupled s-wave BCS superconductivity. On the other hand, $\mu$SR studies have been interpreted as evidence of either one highly anisotropic or two distinct energy gaps.\textsuperscript{8} Furthermore, five-fold and six-fold stacking sequences of (Al, Si) layers corresponding to two different values of $T_c$ of ~6 and ~8 K were found.\textsuperscript{13} Therefore, an experimental study of in- and out-of-plane superfluid density is needed to understand the anisotropic superconducting gap structure and to elucidate the mechanism of superconductivity in AlB$_2$ type compounds.

Single crystals of CaAlSi were grown from Ca:Al:Si (1:1:1) ingots using a floating zone method as described elsewhere.\textsuperscript{18} Samples have $T_c$ either 6.2 or 7.3 K, which is directly related to different stacking sequences.\textsuperscript{13} We measured two of each type of slab-shaped crystals with typical dimensions $0.3 \times 0.3 \times 0.4$ mm$^3$. The penetration depth was measured with an LC tunnel-diode oscillator which is sensitive to changes in the susceptibility of several pico-emu or, equivalently, to changes in the London penetration depth of about 0.3 Å for our crystals.\textsuperscript{16} The quantitative analysis of the frequency shift depends on the sample shape and relative orientation of the excitation field $H_{ac}$ with respect to the principal axes. Assuming a superconducting crystal with an isotropic in-plane response determined by the in-plane penetration depth $\lambda_{ab}(T)$ and possibly different $c$-axis penetration depth $\lambda_c(T)$ at least two experimental arrangements are required to extract $\lambda_{ab}(T)$ and $\lambda_c(T)$ separately. In the $H_{ac} \parallel c$-axis orientation, superconducting currents are generated in the $ab$ plane, thus the susceptibility is determined only by $\lambda_{ab}(T)$ and the frequency shift $\Delta f(T) = f(T) - f_0$ is given by

$$\Delta f(T) = -\frac{f_0 V_0}{2V_0(1 - N)} \left[ 1 - \frac{\lambda(T)}{R} \tanh \left( \frac{R}{\lambda(T)} \right) \right],$$

where $V_0$ is the effective coil volume, $N$ is the demagnetization factor, $\lambda(T)$ is the London penetration depth, and $R$ is the effective planar sample dimension.\textsuperscript{16} With magnetic susceptibility $\chi$ this equation is just $\Delta f(T) = -4\pi\chi(T)\Delta f_0$ where the only sample shape-dependent parameter $\Delta f_0$ is measured directly by pulling the sample out of the coil at a low temperature.

Figure 1 shows the in-plane penetration depth determined from the frequency shift using Eq. (1). The zero-temperature value was estimated from the fit to the BCS formula as described below. This value is not important for the analysis of $\Delta \lambda_{ab}(T)$, but is needed to estimate the superfluid density. Muon spin rotation gives $\lambda_{ab}(0) = 2390 \text{ Å,}^8$ measurements of the critical field $\lambda_{ab}(0) = 3140 \text{ Å,}^9$ and reversible magnetization $\lambda_{ab}(0) = 3100 \text{ Å.}^9$ Our conclusions are not significantly affected by the variation of these values. The main purpose of Fig. 1 is to compare crystals with different $T_c$. The inset shows data on a full temperature scale. The signal saturates at the level corresponding to the normal-state skin depth, thus providing additional information—contactless measurements of the resistivity above the transition. We find 45 and 33 $\mu\Omega$ cm for $T_c = 6.2$ and 7.3 K, respectively, which is in an
agreement with direct measurements on single crystals, which found 36 $\mu$Ω cm on a higher $T_c$ sample. On the contrary, when $\lambda_{ab}(T)$ is plotted versus a reduced temperature $T/T_c$, the curves for the two samples coincide (no normalization was done for the y axis). The open symbols in Fig. 1 show the results for $T_c = 7.3$ K crystal, whereas closed symbols show $T_c = 6.2$ K material. The data are well fit by the standard weak-coupling $s$-wave BCS model

$$\frac{\Delta \lambda(T)}{\lambda(0)} = \sqrt{\frac{\pi \Delta(0)}{2T_c}} \exp \left( -\frac{\Delta(0)}{T} \right),$$

(2)

where, from $\Delta \lambda_{ab}(T)$, we obtained $\Delta_{ab}(0) = 1.76k_BT_c$ a weak-coupling $s$-wave BCS superconducting gap.

In the $H_{ac}\parallel ab$ orientation shielding currents flow along both the $ab$ plane and the $c$ axis. The full magnetic susceptibility is obtained from the anisotropic London equation, which must be solved numerically to extract the interplanar penetration depth $\lambda_c(T)$. For a slab $2b \times 2d \times 2w$ with magnetic field oriented along the longest side $w$ the following solution has been obtained:

$$\frac{\Delta f_c(T)}{\Delta f_{c0}} = 1 - \frac{\lambda_{ab}}{d} \tanh \left( \frac{d}{\lambda_{ab}} \right) - 2\lambda_{ab}^2 \sum_{n=0}^{\infty} \frac{\tanh(\tilde{\beta}_n/\lambda_{ab})}{\tilde{\beta}_n^2},$$

(3)

where $\lambda_{ab}(T)$ from independent measurements in the $H_{ac}\parallel c$ orientation and measuring the total frequency shift upon extraction of the sample from the coil $\Delta f_{c0}^{\text{sh}}$, Eq. (3) is solved numerically to obtain $\lambda_c(T)$.

Figure 2 shows the out-of-plane penetration depth obtained from Eq. (3). The main frame shows the $T_c = 6.2$ K sample, whereas the inset shows data for the $T_c = 7.3$ K sample. The solid lines are the fits to the low-temperature isotropic BCS expression, Eq. (2). The gap amplitude obtained from the fits indicates stronger coupling along the $c$ axis [comparable to the $\lambda_{ab}(T)$ fits, Fig. 1]. However, as shown below, such fitting significantly underestimates the anisotropy of the superconducting gap. The major problem is that Eq. (2) is only valid for an isotropic gap that is constant with temperature, restricting its range of validity to $T/T_c<0.35$. This restriction excludes a significant portion of the data. A more comprehensive analysis requires a determination of the normalized superfluid density, which is obtained from the measured change in the penetration depth $\Delta \lambda(T)$ via $\rho(T) = \left[ 1 + \Delta(0)/\lambda(0) \right]^{-2}$.

The superfluid density generally depends on the shape of the Fermi surface and the gap anisotropy. For CaAlSi we can assume a fairly isotropic Fermi surface, a superconducting gap isotropic in the $ab$ plane, and anisotropic for the out-of-plane response. Within the semiclassical approximation,  

$$\rho_c = 1 - \frac{3}{2T} \int_0^1 (1-z^2) \left[ \int_0^\infty \cosh^{-2} \left( \frac{\sqrt{\epsilon^2 + \Delta(z)^2}}{2T} \right) d\epsilon \right] dz,$$

(4)

$$\rho_{ab} = 1 - \frac{3}{4T} \int_0^1 (1-z^2) \left[ \int_0^\infty \cosh^{-2} \left( \frac{\sqrt{\epsilon^2 + \Delta(z)^2}}{2T} \right) d\epsilon \right] dz,$$

(5)

where $z=\cos(\theta)$ and $\theta$ is the polar angle with $\theta=0$ along the $c$ axis. Since there is no general argument for the shape of the gap, we choose the spheroidal form

$$\Delta(T,\theta) = \frac{\Delta_{ab}(T)}{\sqrt{1-e^2 \cos^2(\theta)}},$$

(6)

and parameter $-\infty < e \leq 1$ is related to eccentricity $e$ as $e = e^c = 1-c^{-1}$ where $c$ is the normalized semiaxis along the $c$ axis, but $e$ can assume both negative and positive values. The spheroid is either prolate ($e>0$), oblate ($e<0$), or a sphere ($e=0$). The temperature dependence of the superconducting gap was obtained from the anisotropic gap equation. We found that it is well approximated by $\Delta(T) = \Delta(0) \tanh(1.785/T_c/T-1)$. 

FIG. 1. (Color online) Low-temperature variation of the in-plane penetration depth in two crystals plotted versus reduced temperature $T/T_c$. The Red line is a fit to a low-temperature $s$-wave BCS model, Eq. (2). The inset shows a full temperature scale along with the normal state resistivities extracted from the skin depth.
The following data analysis was performed. By measuring the same sample in two orthogonal orientations (along the c axis and along the ab plane), both $\lambda_{ab}(T)$ and $\Delta_f$ were obtained. The latter contains contributions from both $\lambda_{ab}(T)$ and $\lambda_c(T)$. Equation (3) was then used to numerically evaluate $\lambda_c(T)$. Low-temperature BCS fits as well as measurements of the reversible magnetization were used to estimate $\lambda_{ab}(0)=0.31 \mu m$ and $\lambda_c(0)=0.65 \mu m$. Fits over the full temperature range confirmed the assumed values. Then Eqs. (4) and (5) were used to fit the data. As a final step, both curves $\rho_{ab}(T)$ and $\rho_c(T)$ were generated from a single set of fitting parameters.

Figure 3 shows data and fitting results for the lower $T_c =6.2$ K samples. Symbols are the measured data points and solid lines are calculated for the ellipsoidal gap shown in the inset. The fitting procedure yielded the weak-coupling BCS value $\Delta_{ab}(0)/k_B T_c=3.53$ in the ab plane and $\varepsilon=0.656$ corresponding to $\Delta_c(0)/k_B T_c=6.02$ gap maximum along the c axis.

Figure 4 shows similar results for the samples with $T_c =7.3$ K. There is an obvious reduction of the gap anisotropy. The best fit to the ellipsoidal gap yields $\varepsilon=0.206$ resulting in $\Delta_c(0)/k_B T_c=3.98$. It should be noted that in most previous works only averaged values of the superconducting gap could be obtained. From heat capacity measurements, $\Delta(0)/k_B T_c=4.07$ was obtained, whereas ARPES yielded $\Delta(0)/k_B T_c=4.2^{+10}$. The average effective gap can be obtained from our results by equating volumes of the spherical gap and a sphere, $\Delta_{eff}=\Delta_{ab}(0)(1-\varepsilon)^{-1/6}$. This gives $\Delta_{eff}(0)/k_B T_c=4.22$ for samples with $T_c =6.2$ K and $\Delta_{eff}(0)/k_B T_c=3.66$ for samples with $T_c =7.3$ K which is in the correct range of reported values and our earlier fits using Eq. (2). All these values should be compared to the weak-coupling isotropic result of $\Delta(0)/k_B T_c=3.53$.

For all samples studied, we find that the temperature dependencies of both in-plane and out-of-plane superfluid density are fully consistent with single-gap anisotropic s-wave superconductivity. The gap magnitude in the ab plane is close to the weak-coupling BCS value while the c axis values are somewhat larger. Our results suggest that scattering is not responsible for the difference in $T_c$. Scattering would lead to a suppression of the gap anisotropy. The gap with average value $\Delta$ and variation $\delta\Delta$ on the Fermi surface can only survive if $h \tau^{-1} \ll \sqrt{\Delta \delta\Delta}$, where $\tau$ is the impurity scattering rate. The values of resistivity are very close for both high- and low-$T_c$ samples (45 and 33 $\mu\Omega$ cm, respectively); see Fig. 1, the qualitative trend in anisotropy is just opposite. Also, 15% suppression of $T_c$ by nonmagnetic impurities requires very large concentrations. This would, indeed, significantly smear the transition, which we did not observe. Therefore, all facts point out that in a CaAlSi gap anisotropy abruptly decreases as $T_c$ abruptly increases from ~6 to ~8 K. A plausible mechanism comes from the analysis of the stacking sequence of (Al/Si) hexagonal layers. There are two structures—five-fold and six-fold stacking corresponding to low- and high-$T_c$ samples, respectively. The buckling of (Al,Si) layers is greatly reduced in a six-fold structure, which leads to the enhancement of the density of states, hence higher $T_c$. Our results suggest that reduced buckling also leads to almost isotropic gap function. This may be due to significant changes in the phonon spectrum and anisotropy of the electron-phonon coupling.

Measurements of the field dependence of the penetration depth in the vortex state also show a difference between the two sets of samples, as do measurements taken with different field orientations relative to the c axis. Of particular interest is the variation of the second critical field and the so-called peak effect. Tunnel-diode studies of these properties will be reported elsewhere.

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