Upper critical field of Ti and α-TiAl alloys: Evidence of an intrinsic type-II superconductivity in pure Ti

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The upper critical field H_{c2} of α-$Ti_{1-x}Al_x(0 \leqslant x \leqslant 0.1)$ alloys has been investigated in detail. The behaviors can well be described by the theory of type-II superconductors. The electronic specific heat deduced from the superconducting properties is in excellent agreement with previous calorimetric measurements. However, the Fermi velocity obtained here is substantially lower than predicted by band calculation. The present work gives clear evidence that pure Ti is an intrinsic type-II superconducting element due to its very low renormalized Fermi velocity.

The theoretical understanding of conventional superconductivity has had great triumph as we now not only know the basic microscopic mechanism of its occurrence, but also can often be successful in correlating the superconducting properties of a specific material with its thermodynamical and microscopic parameters.[1] The experimental demonstration of the success is, however, mostly biased to materials with cubic structures because of their importance for application. Comparatively, much less data were accumulated for metals of, say, *hcp* structure which usually have very low superconducting transition temperature T_c. Therefore, detailed measurements of the superconducting properties on these materials in themselves could be very valuable in balancing our knowledge on the phenomenon. Here we report a systematic investigation of the upper critical field H_{c2} of a series of *hcp* $Ti_{1-x}Al_x(0 \leqslant x \leqslant 0.1)$ alloys. The system was chosen for the following additional reasons: (1) The *hcp* α-TiAl phase is stable up to $\sim$11 at. % Al. In the whole doping range, the lattice parameters change very little. The widths of the x-ray diffraction peaks do not show appreciable degradation by introducing 10 at. % Al.[2] (2) Band-structure calculation shows that the addition of Al into α-Ti does not disturb the *d*-band structure. Adding 10 at.% Al only slightly shifts the Fermi energy and causes a mere density of states (DOS) decrease of $\sim$7%.[3] (3) T_c of α-TiAl alloy is very low, leaving enough room for independent measurements of the normal properties related to the superconductivity of the materials. Since the residual resistivity ρ_0 of the alloy changes by about two orders between pure Ti and $Ti_{0.9}Al_{0.1}$, it provides a very clean case for the investigation of how the theory works in the wide range from clean limit to dirty limit by nearly a mere change of scattering rate. The present measurements are in excellent consistency with the theory for type-II superconductors. The results give unambiguous evidence that pure Ti is an intrinsic type-II superconductor due to its very low renormalized Fermi velocity.

The α-$Ti_{1-x}Al_x$ samples were prepared by arc melting with Al concentration up to 10 at. %. Appropriate amount of Ti (99.995% pure) and Al (99.999% pure) were arc melted several times. The melted ingots were then annealed at 900 °C for one week.[4] X-ray diffraction with very sharp peaks shows that all the samples had well crystallized single-phase *hcp* structure without preferential orientation.[2] The lattice parameters slightly decrease by introducing Al with very small anisotropy. The relative changes of the lattice parameters between pure Ti and $Ti_{0.9}Al_{0.1}$ are about 0.5% for $\Delta a/a$, and $\sim$0.2% for $\Delta c/c$. We will ignore the anisotropy in the follwing treatment.[5] We expect that this simplification does not influence the main conclusion of the paper as no preferential orientiation exists in our samples and therefore the equivalent isotropic average should be on equal footing for different samples.

The experiments were conducted in a dilution refrigerator with a superconducting magnet. The preliminary result of the T_c change with Al concentration were reported elsewhere.[2] The critical field was determined by the middle points of resistivity change in a sweeping field using four-lead ac measurements. The relative widths of the transition (10–90 %)

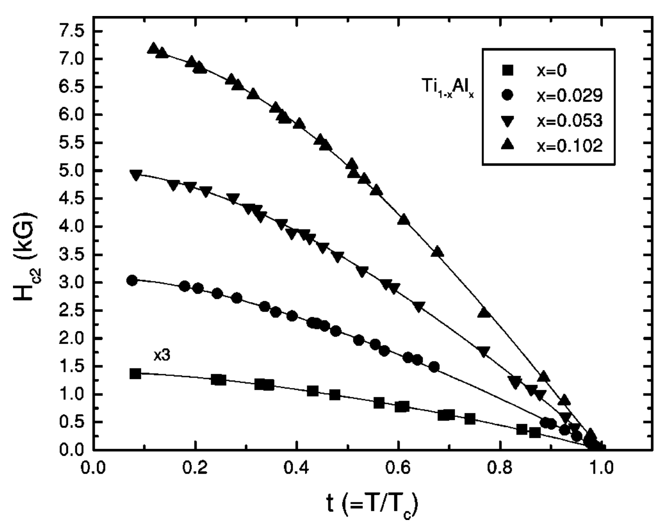

FIG. 1. Upper critical field $H_{c2}(t)$ as a function of reduced temperature $t = T/T_c$ for α-$Ti_{1-x}Al_x$ alloys with $x = 0$, 0.029, 0.053, and 0.102.

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were ∼10% or less for all the samples at very low temperature, the uncertainty rises to ∼14% near T_c. The temperature was very slowly swept from ∼40 mK to the zero field T_c of the samples. As will be demonstrated below, the measured critical field is actually the upper critical field H_{c2} of the samples. Different criterion (80%, 50%, and 20% of the transition) lead to a fluctuation of $\sim\pm5\%$ in H_{c2} and less than $\sim\pm5\%$ in $dH_{c2}/dT|_{T_c}$.

Four samples were measured and the results are shown in Fig. 1. A collection of the data together with the samples' normal-state resistivities are listed in Table I. The behavior of a type-II superconductor has been successfully described by the Ginzburg-Landau-Abrikosov-Gorkov (GLAG) theory, especially near T_c, where the following relationship precisely holds:[6]

$$-\left.\frac{dH_{c2}}{dT}\right|_{T_c}=\frac{\eta_{H_{c2}}(T_c)}{R(\lambda_{tr})}\left[\left(\frac{24\pi^2}{7\zeta(3)}\frac{k_B^2c}{\hbar e}\right)\frac{T_c}{v_F^{*2}}+\left(\frac{12\pi}{7\zeta(3)}\frac{k_Bc}{e}\frac{1}{v^*l}\right)\right]$$
$$=\frac{\eta_{H_{c2}}(T_c)}{R(\lambda_{tr})}\left[3.18\times10^{16}\frac{T_c}{v_F^{*2}}+5.26\times10^4\gamma^*\rho_0\right] \quad (1)$$

where $\eta_{H_{c2}}(T_c)$ is the ratio of the strong-coupled magnetic pair-breaking parameter to the weak-coupled BCS value, λ_{tr} is about the ratio of the zero-temperature GL coherence length $\xi_{GL}(0)$, the transport scattering length l, $R(\lambda_{tr})$ is a function weakly depending on λ_{tr} $[R(0)=1,R(\infty)=1.17]$, v_F^* in cm/s and γ^* in erg/cm^{3}K^2 are, respectively, the renormalized Fermi velocity and electronic specific-heat coefficient, and ρ_0 in Ω cm is the residual resistivity. Since $\eta_{H_{c2}}(T_c)$ is close to unity and the deviation depends on the ratio of $(T_c/\omega_0)^2$, where ω_0 is the equivalent Einstein frequency, we expect $\eta_{H_{c2}}(T_c)=1$ for our α-TiAl samples. To see whether our α-TiAl samples can be described by GLAG theory, Eq. (1) can be written as

$$\frac{R(\lambda_{tr})}{T_c}\left.\frac{dH_{c2}}{dT}\right|_{T_c}=3.18\times10^{16}v_F^{*-2}+5.26\times10^4\gamma^*\frac{\rho_0}{T_c}, \quad (2)$$

taking $\eta_{H_{c2}}(T_c)=1$. We see, by plotting $[R(\lambda_{tr})/T_c](dH_{c2}/dT)|_{T_c}$ as a function of ρ_0/T_c, that we should get a straight line if v_F^* and γ^* are independent of doping. The result is shown in Fig. 2. The fitting curve slightly bends down from a straight line. However, if we take into account the Al-induced decrease of DOS,[3] then the correction factor would straighten the curve to coincide with the dashed line of the figure. Since we have no adjustable parameter in the treatment, the excellent agreement between our data with Eq. (2) demonstrates that introducing Al into α-Ti does not appreciably change the band Fermi velocity v_F as well as the electron-phonon coupling λ_{ep}, in agreement with the fact that no topological defects are introduced in the process. According to Eq. (2), from the slope we can get the renormalized electronic specific-heat coefficient, which gives $\gamma^*\sim3$ mJ/cm^3 K^2, in satisfactory consistency with calorimetric data ($\gamma^*\sim3.15$ mJ/cm^3 K^2).[7] The intercept leads to the renormalized Fermi velocity $v_F^*\sim4.1\times10^6$ cm/s, a value substantially lower than predicted by the band calculation ($\sim2.2\times10^7$).[8] To check the correctness of the result, we notice that we could have more precise conclusion from the $H_{c2}(0)$ data. It is easy to write down the relation:[9]

TABLE I. A list of the measured data for the α-Ti$_{1-x}$Al$_x$ alloys.

x	ρ_0 ($\mu\Omega$ cm)	ρ_{300}/ρ_0	T_c (K)	$H_{c2}(0)$ (kG)[a]	$dH_{c2}/dT\|_{T_c}$ (kG/K)[b]
0	2.25	22.2	0.49	0.46[5]	1.3
0.029	40	2.1	0.65	3.05	6.9
0.053	68	1.6	0.7	5	11.3
0.102	113	1.2	0.73[5]	7.28	16

[a]Extrapolated to $T=0$ by polynomial fitting of the data.
[b]Obtained by polynomial fitting.

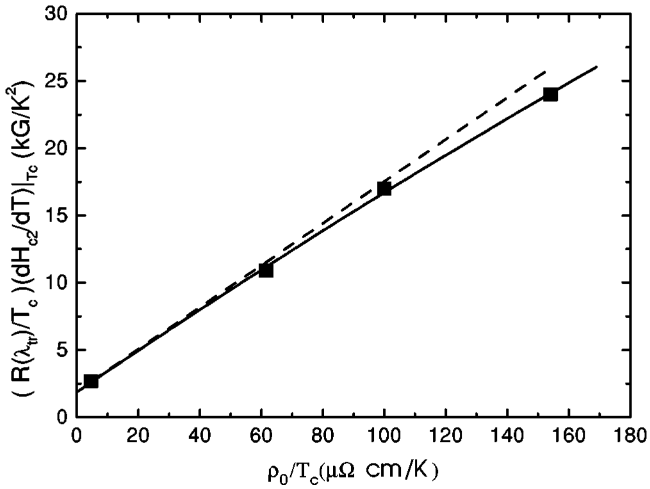

FIG. 2. $[R(\lambda_{tr})/T_c](dH_{c2}/dT)|_{T_c}$ as a function of ρ_0/T_c. The dashed line is the slope at $\rho_0\to0$. When the change of γ^* with Al concentration is taken into account, all the data points fall on the dashed line. The slope of the dashed line gives the electronic speific-heat coefficient γ^* of pure Ti, while the intercept gives the Fermi velocity v_F^* (see text).

$$H_{c2}(0)=\frac{\phi_0}{2\pi\xi_{GL}^2(0)}=\frac{\phi_0}{2\pi}\left[\frac{12}{7\zeta(3)}\frac{4\pi^2k_BT_c^2}{\hbar^2v_F^{*2}}\right]\frac{(1+\lambda_{tr})}{R(\lambda_{tr})}, \quad (3)$$

where ϕ_0 is the flux quantum and $\xi_{GL}(0)$ is zero-temperature Ginzburg-Landau coherence length. Similar to Eq. (2), we can modify Eq. (3):

$$\frac{H_{c2}(0)}{T_c^2}=3.17\times10^{15}v_F^{*-2}+3.06\times10^4\gamma^*\frac{\rho_0}{T_c}. \quad (4)$$

When we plot $H_{c2}(0)/T_c^2$ as a function of ρ_0/T_c (Fig. 3), we get behavior that is very similar to Fig. 2. The results give $\gamma^*\sim3.1$ mJ/cm^3 k^2 and $v_F^*\sim4.6\times10^6$ cm/s. Again, γ^* is in excellent agreement with [7] and v_F is in reasonable agreement with that obtained by the H_{c2} slope at T_c.

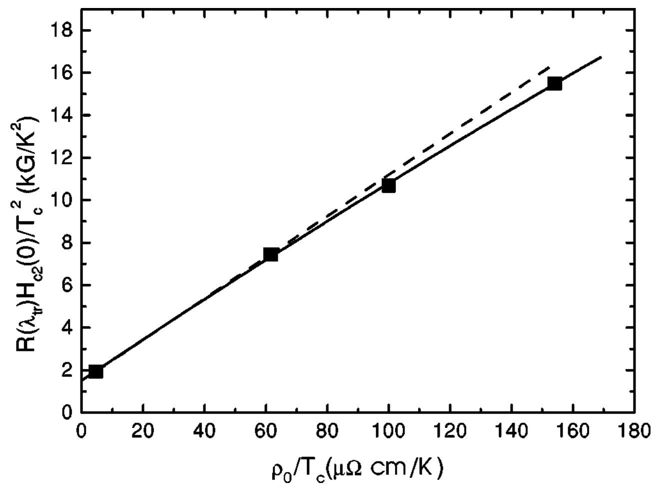

FIG. 3. $R(\lambda_{tr})H_{c2}(0)/T_c^2$ as a function of ρ_0/T_c. The behavior is very similar to that in Fig. 2.

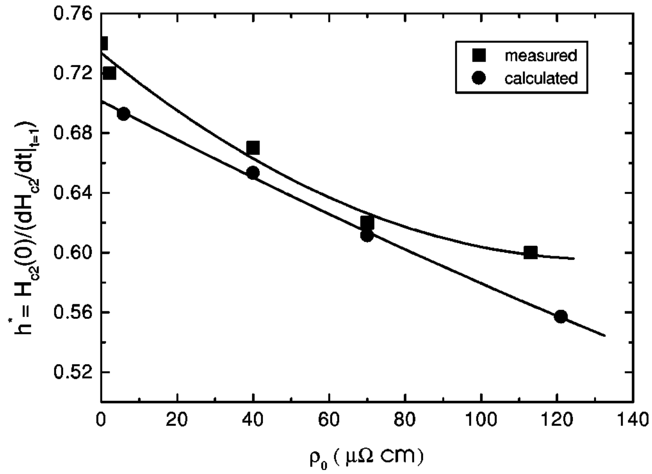

FIG. 4. The change of the reduced upper critical field at $T=0$, $h_{c2}^{d1}(0)=H_{c2}^{d1}(0)/(dH_{c2}^{d1}/dt)|_{t=1}$, with residual resistivity ρ_0 of the samples in the dirty limit. The spin paramagnetism limitation shows up with the increase of ρ_0, in general accordance with the WHH model.

The success of GLAG relationships in describing our α-TiAl samples and the constant v_F^* for different samples allows us to separate $H_{c2}(0)$ and $dH_{c2}/dT|_{T_c}$ into two parts which, according to Eqs. (2) and (4), correspond, respectively, to the values in clean limit and dirty limit:

$$R(\lambda_{tr})H_{c2}^{c1}(0)=3.17\times10^{15}v_F^{*-2}T_c^2,$$

$$R(\lambda_{tr})H_{c2}^{d1}(0)=3.06\times10^{4}\gamma^*\rho_0 T_c \tag{5}$$

and

$$R(\lambda_{tr})\left.\frac{dH_{c2}^{c1}}{dT}\right|_{T_c}=3.18\times10^{16}v_F^{*-2}T_c,$$

$$R(\lambda_{tr})\left.\frac{dH_{c2}^{d1}}{dT}\right|_{T_c}=5.26\times10^{4}\gamma^*\rho_0. \tag{6}$$

Then we may compare the data deduced from Eqs. (5) and (6) with a formula applicable in the two extremes. A familiar result is that in the clean limit $H_{c2}(0)=0.73(dH_{ch}/dT)|_{T_c}$, while in the dirty limit $H_{c2}(0)=0.69(dH_{c2}/dT)|_{T_c}$.[10] The spin paramagnetism, however, will limit H_{c2} and reduce the ratio of $h_{c2}(0)$ and $dH_{c2}/dT|_{T_c}$.[11] The effect should manifest itself with the increase of ρ_0. Indeed, we find that in dirty limit the reduced upper critical field $h_{c2}^{dl}(0)\equiv H_{c2}^{dl}(0)/(dH_{c2}/dT)|_{T_c}$ shows a decrease for high ρ_0, in reasonable agreement with that calculated according to the Werthamer-Helfand-Hohenberg (WHH) WHH model[11] (Fig. 4). In the calculation, the spin-orbit coupling λ_{s0} was chosen to be small ($\lambda_{s0}\sim0.2T_c^{-1}$) according to Ref. 12 where the spin-orbit relaxation time was determined to be 8×10^{-12} and is nearly independent of Al concentration. In the clean limit, $h_{c2}(0)$ is almost independent of ρ_0 and is indeed close to 0.73. No anisotropy-enhanced $h_{c2}(0)$ (Ref. 13) was detected in our samples, proving that the isotropic approximation is acceptable in the treatment.

We are not trying to stress too much about the quantitative agreement of our data with a typical type-II superconductor. The experimental uncertainty in determining $dH_{c2}/dT|_{T_c}$ and the approximation in the $H_{c2}(0)$ expression do not allow us to do so. However, the agreement without any adjustable parameter is certainly not a fortuity. It gives convincing evidence of the very low renormalized Fermi velocity for pure Ti and α-TiAl alloys which one should treat seriously. The result is not so unreasonable, considering that Ti is one of the most ''resistive'' elements, its DOS is at a minimum, and its electron-phonon coupling estimated by re-

TABLE II. Superconducting parameters of TiAl alloys as a function of residual resistivity ρ_0.

ρ_0 ($\mu\Omega$ cm)	T_c (K)	ξ_0 (Å)	$\lambda_L(0)$ (Å)	$\kappa(0)$	$H_{c2}^{cl}(0)$ (kG)	$\left.\frac{dH_{c2}^{cl}(0)}{dT}\right\|_{T_c}$ (kG/K)	$h_{c2}^{*cl}(0)$	$H_{c2}^{dl}(0)$ (kG)	$\left.\frac{dH_{c2}^{dl}}{dT}\right\|_{T_c}$ (kG/K)	$h_{c2}^{*dl}(0)$
0	0.41[a]	1500	3100	2.1	0.24	0.8	0.74			
2.25	0.49	1150	3100	3.9	0.34	0.94	0.73	0.12[5]	0.36[5]	0.72
40	0.65	870	3100	22	0.59	1.24	0.73	2.43	5.65	0.67
70	0.7	800	3100	36	0.69	1.33	0.73	4.31	10	0.62
113	0.73[5]	760	3100	55	0.75	1.4	0.73	6.53	14.8	0.6

[a]Extrapolated to $\rho_0=0$; ξ_0 is the coherence length in the clean limit; $\lambda_L(0)$ is the London penetration depth at 0 K, $\kappa(0)$ is the zero-temperature Ginzburg-Landau parameter.

sistivity could be the largest among the transition metals.[1] We will leave the matter to future theoretical and experimental investigations. A very important, though surprising, consequence of this very low v_F^* is that pure Ti is actually an intrinsic type-II superconducting element, contrary to previous conclusions. The evidence for this conclusion is so strong that it can never be ascribed to the limited precision of the expressions and is far beyond the uncertainty of the measurements. A collection of the superconducting parameters as a function of residual resistivity is listed in Table II.

In summary, by introducing Al into α-Ti, we were able to change the impurity scattering rate by almost two orders with the topological lattice structure and electronic band structure least perturbed. The alloys provided a clean case where we can demonstrate that the theory of type-II superconductors is applicable to α-TiAl alloys in a very wide range from the clean limit to dirty limit. The results give convincing evidence that pure Ti is an intrinsic type-II superconductor with the lowest T_c up to now due to its very low renormalized Fermi velocity.

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