Thermodynamics of MgB_2 described by the weak-coupling two-band BCS model

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Based on weak-coupling anisotropic BCS theory, the temperature dependence of energy gap and the specific heat are evaluated for the MgB_2 superconductor, and the results are compared with experimental data. We show that the weak-coupling anisotropic BCS theory describes thermodynamic experimental data with high precision, 3–6%.

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A keen interest excited by discovery and experimental investigation of a new high T_c superconductor MgB_2 is to a large extent associated with its dissimilarity to cuprate superconductors. The superconductivity of MgB_2 is definitely a three-dimensional effect, whereas in cuprates it is presumably two-dimensional (2D). Nevertheless, the superconducting gap in MgB_2 displays strong anisotropy. The most precise tunneling measurements by Gonnelli *et al.*[1] give the value 2.6 for the ratio of the gaps at two conductivity bands. On the other hand, the measured gaps are the same for the tunneling in the *ab*-plane and in the *c*-direction, indicating that they do not depend on direction within each piece of the Fermi surface.

An important problem is how strong is the interaction in MgB_2. First-principles calculations[2–4] indicate that electron-phonon interaction is not weak and that the Eliashberg description is appropriate. However, anisotropy and interaction were shown to influence thermodynamics oppositely. For example, the anisotropy decreases the relative discontinuity of the specific heat at the transition point,[5,6] whereas the first correction due to interaction increases it.[7] Besides, MgB_2 is a very hard material with a high value of Debye frequency, which usually correlates with a weak coupling. Therefore it is not *a priori* clear what is more substantial in the case of MgB_2.

The purpose of our work is to demonstrate that the anisotropy effects are more substantial at least for thermodynamic measurements. We show that, as a matter of fact, the weak coupling anisotropic BCS theory describes all known thermodynamic experimental data including the temperature dependence of the energy gap and specific heat with a high precision, 3–6%.

The main features of the anisotropic weak coupling BCS model were elucidated in the early 1960s,[5,6,8–10] the ultimate result being the factorization of the gap[5]

$$\Delta(T,\mathbf{k}) = Q(T)\chi(\mathbf{k}), \tag{1}$$

which was experimentally verified by Zavaritskii.[11] The function of angle $\chi(\mathbf{k})$ is the eigenfunction of the interaction operator $V(\mathbf{k},\mathbf{k}')$ corresponding to the maximal eigenvalue λ_+. It satisfies the linear homogeneous integral equation:

$$\int V(\mathbf{k},\mathbf{k}')\chi(\mathbf{k}')\frac{d\sigma'}{v_F v_F} = \lambda_+\chi(\mathbf{k}). \tag{2}$$

Integration in Eq. (2) proceeds over the Fermi surface with $d\sigma = dS/8\pi^3$ with dS being a differential area of the Fermi surface; $\nu_F = \int d\sigma / v_F$ is the electron density of the state per spin at Fermi level. The function $\chi(\mathbf{k})$ is normalized as follows:

$$\langle \chi^2(\mathbf{k}) \rangle = 1. \tag{3}$$

The angular average value $\langle X \rangle$ is $\langle X \rangle = \int X d\sigma / \nu_F$. The temperature dependent factor $Q(T)$ can be found from the orthogonality condition:

$$\ln\frac{Q(0)}{Q(T)} = \left\langle \chi^2(\mathbf{k}) F\left(\frac{Q(T)\chi(\mathbf{k})}{T}\right)\right\rangle, \tag{4}$$

where

$$F(x) = \int_{-\infty}^{+\infty} \frac{du}{\sqrt{x^2+u^2}(\exp\sqrt{x^2+u^2}+1)}. \tag{5}$$

The value $Q(0)$ is associated with the transition temperature T_c by the following relationship:

$$\frac{Q(0)}{T_c} = \frac{\pi}{\gamma}\exp[-\langle \chi^2(\mathbf{k})\ln|\chi(\mathbf{k})|\rangle], \tag{6}$$

here $\gamma = e^C = 1.781072\ldots$ and C is Euler's constants. The specific heat $C(T)$ reads

$$C(T) = 2\nu_F T\frac{d}{dT}\left\langle \Delta_{\mathbf{k}} G\left(\frac{\Delta_{\mathbf{k}}}{T}\right)\right\rangle, \tag{7}$$

where $G(x) = 2x\int_0^\infty \cosh(2\varphi)F(x\cosh\varphi)d\varphi$.

We now apply these formulas to MgB_2. The Fermi surface of MgB_2 has two σ-type 2D cylindrical hole sheets and two π-type three-dimensional tubular networks.[12,13,16,17] We accept a simple model introduced first by Moskalenko[14] and Suhl *et al.*,[15] in which the interaction does not depend on the momentum inside each band, but only on the band index. Thus it can be written as a 2×2 Hermitian matrix V_{ik} $(i,k = \sigma,\pi)$. The order parameter (energy gap) in each band in such a model does not depend either on the momentum

within each band and can be described by a 2D vector with components Δ_σ, Δ_π. The validity of this simple model is supported by the tunneling measurements of the energy gap,[1] which displays the same values for two gaps in the *ab*-plane and in the *c*-direction. The normalized wave function of the Cooper pairs $\chi_{\mathbf{k}}$ has the same property: $\chi_\sigma(\mathbf{k})=\chi_\sigma$, $\chi_\pi(\mathbf{k})=\chi_\pi$, where χ_σ and χ_π are two constants. We introduce an additional simplification assuming these constants to be real. Let us denote the density of states in the σ and π bands as $\nu_{F\sigma}$ and $\nu_{F\pi}$, respectively. Then the definition of an average value $\langle X\rangle$ for any physical value X, which does not change within each band reads

$$\langle X\rangle = X_\sigma c_\sigma + X_\pi c_\pi, \tag{8}$$

where c_σ and c_π are statistical weights of the bands $c_\sigma=\nu_{F\sigma}/\nu_F$ and $c_\pi=\nu_{F\pi}/\nu_F$, $\nu_F=\nu_{F\sigma}+\nu_{F\pi}$. The general normalization condition Eq. (3) for this model reads

$$\chi_\sigma^2 c_\sigma + \chi_\pi^2 c_\pi = 1. \tag{9}$$

Equation (6) can be written explicitly as follows:

$$\frac{Q(0)}{T_c} = \frac{\pi}{\gamma\chi_{\mathrm{av}}}, \tag{10}$$

where $\chi_{\mathrm{av}}=\chi_\sigma^{2c_\sigma}\chi_\pi^{2c_\pi}$. We assume the values $c_\sigma=0.44$ and $c_\pi=0.56$ as found from density-functional theory calculations in Refs. 12, 13, and 16. The second fitting parameter is T_c. There is no experimental discrepancy on this value, and it is commonly accepted to be $T_c\approx 39$ K. One additional fitting parameter for the two-band theory is the ratio $\delta=\chi_\sigma/\chi_\pi$. We have extracted it from the tunneling gap measurements[1] extrapolating them to zero temperature:

$$\delta=\chi_\sigma/\chi_\pi \approx 2.54. \tag{11}$$

Equations (9) and (11) allow us to determine χ_σ and χ_π separately: $\chi_\sigma=\delta/\sqrt{c_\sigma\delta^2+c_\pi}=1.38$; and $\chi_\pi=1/\sqrt{c_\sigma\delta^2+c_\pi}=0.54$. According to the weak-coupling theory, the ratio δ must be the same at any temperature. This crucial condition is satisfied in the tunneling experiment[1] with all experimental precision.

For the temperature dependence of the gap in the BCS two-band model, we find from Eq. (4):

$$-\ln q = \chi_\sigma^2 F\left(\frac{\pi\chi_\sigma q}{\gamma\chi_{\mathrm{av}}t}\right)c_\sigma + \chi_\pi^2 F\left(\frac{\pi\chi_\pi q}{\gamma\chi_{\mathrm{av}}t}\right)c_\pi. \tag{12}$$

Here $q(t)=Q(t)/Q(0)$ and $t=T/T_c$. $F(x)$ is defined by Eq. (5). The graph of the function $q(t)$ is shown in Fig. 1 by the solid curve. The dashed curve in Fig. 1 represents $q(t)$ in the isotropic single-gap model (standard BCS model). The graphs of the energy gaps $\Delta_\sigma=Q(t)\chi_\sigma$ and $\Delta_\pi=Q(t)\chi_\pi$ versus T/T_c are shown in Fig. 2 together with the experimental data,[1] which agree with theory within the limits of experimental uncertainty.

The specific heat in the two-band model is given by the following equation directly stemming from Eq. (7):

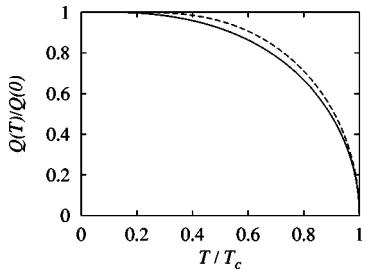

FIG. 1. The solid curve depicts the ratio $Q(T)/Q(0)$ vs $t=T/T_c$ for the two-band model; the dashed curve is the same value for the standard (isotropic) BCS theory.

$$\frac{C(T)}{C_N(T)} = c_\sigma r_c(y_\sigma) + c_\pi r_c(y_\pi) + \frac{12}{7\zeta(3)}\frac{[c_\sigma\chi_\sigma^2 r_a(y_\sigma)+c_\pi\chi_\pi^2 r_a(y_\pi)]^2}{c_\sigma\chi_\sigma^4 r_b(y_\sigma)+c_\pi\chi_\pi^4 r_b(y_\pi)}, \tag{13}$$

where $C_N(T)=\gamma T$ is the specific heat for the normal metal; $y_\sigma=\pi/2\gamma\, q/t\,\chi_\sigma/\chi_{\mathrm{av}}$, and $y_\pi=\pi/2\pi q/t\chi_\pi/\chi_{\mathrm{av}}$. The functions r_i are defined by integrals $r_i(x)=\int_{-\infty}^{+\infty} g_i(\sqrt{x^2+y^2})dy$, $i=a, b, c$, where g_i read:

$$g_a(x) = \frac{1}{2\,\cosh^2(x)},$$

$$g_b(x) = \frac{\pi^2}{14\zeta(3)}\left(\frac{\tanh x}{x} - \frac{1}{\cosh x}\right)\frac{1}{x^2},$$

$$g_c(x) = \frac{6}{\pi^2}\frac{x^2}{\cosh^2 x}. \tag{14}$$

For technical details related to this calculation see Mishonov *et al.*;[18] the functions g_i were introduced and graphically presented in Ref. 19.

The jump of the specific heat at T_c reads (cf. Refs. 5 and 14):

$$\frac{\Delta C(T_c)}{C_N(T_c)} = \frac{12}{7\zeta(3)}\frac{(\chi_\sigma^2 c_\sigma+\chi_\pi^2 c_\pi)^2}{\chi_\sigma^4 c_\sigma+\chi_\pi^4 c_\pi}. \tag{15}$$

For the data specified earlier, we find $\Delta C(T_c)/C_N(T_c)=0.874$. It agrees with the high precision measurements by Bouquet *et al.*[20] with about 3% precision. In Fig. 3 the ratio

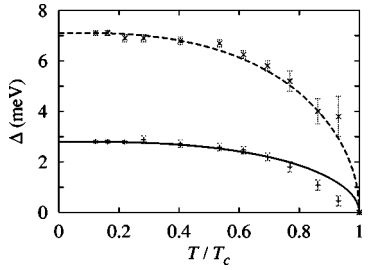

FIG. 2. The solid curve is the theoretical graph of Δ_σ vs T/T_c; the dashed curve is the same for Δ_π; "+" and "×" represent experimental data by Gonnelli *et al.* (Ref. 1).

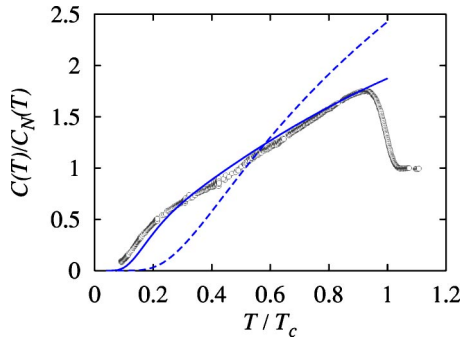

FIG. 3. The solid curve is the theoretical graph of the specific heat for the two band MgB_2 vs $t=T/T_c$; the circles are the experimental data due to Bouquet *et al.* (Ref. 20); and the dashed curve is the theoretical plot of the specific heat given by the isotropic BCS theory.

$C(T)/C_N(T)$ versus T/T_c is plotted. The solid curve is the prediction of the two-band weak coupling theory; the dots are experimental data by Bouquet *et al.*,[20] courteously sent to us by the authors. The theoretical graph $C(T)/C_N$ versus T/T_c agrees well with the experimental data everywhere except for a range of low temperature $T/T_c \leqslant 0.2$. The discrepancy most probably is caused by a relatively small variation of the gap within one band. The specific heat at low temperature is proportional to $e^{-\Delta_{\min}/T}$, whereas the tunneling measurements give the value of the gap along the direction of the tunneling. Given the value of discrepancy, we can estimate the variation of the gap $\bar{\Delta}-\Delta_{\min} \sim 0.1$–$0.15 T_c \ln 2 \approx 3.3$–$4.2$ K. It is about 8–12% of the value of the smaller gap.

Another group of available experimental thermodynamic data relates to magnetic properties: the energy gaps in external magnetic field[21] and the dependence of the second critical field on temperature.[22] The dependence of H_{c2} on temperature was considered theoretically in the framework of the anisotropic BCS model by two groups of authors[23,24] based on the classical approach by Helfand and Wertheimer.[25] Unfortunately, a consistent solution of these problems at any temperature between 0 and T_c requires much more detailed knowledge about the Fermi surface. For example, to reach a satisfactory convergence Miranović *et al.*[23] were forced to introduce 11 different parameters characterizing the Fermi surface and electron interaction. It is clear that our real knowledge of the Fermi surface is too poor for such a sophistication. Dahm and Schopohl[24] applied a simplified model of the Fermi surface as consisting of a torus and cylinder characterized by four parameters only and assumed a plausible variational procedure introducing one more parameter. As it could be expected from the results by Miranović *et al.*, the number of parameters is too small to ensure a reasonable precision. Indeed, a satisfactory agreement with the experiment in Ref. 24 is reached at the expense of a rather exotic choice of parameter. Summing up, the magnetic properties can not be described by such an elementary theory as described above two-band BCS model and require a much more sophisticated approach even in the weak coupling approximation.

Let us discuss why this simplified theory works so well. Let us start from the assumption supported by experiments that the gap does not vary within each band. The in-band isotropy of the gap could be a result of sufficiently strong in-band scattering. At the scattering time $\tau \sim 10^{-14}$ s, i.e., at the residual resistance larger than $10^{-5}\ \Omega$ cm, the energy gap becomes isotropic. However, the ratio of the gaps for different bands still remains bigger than 2 indicating that the interband scattering must be much weaker. It should be emphasized that it is the density of states which becomes isotropic, whereas the order parameter remains anisotropic unless the Ioffe-Regel limit $\tau\varepsilon_F \sim 1$ of the scattering rate is reached.[26] The tunneling experiment measures just the density of state.

The second question is why the weak-coupling model gives such high accuracy. Two different aspects must be enlightened. First, the separability of variables for the order parameter, even in the framework of the weak-coupling approximation, has the precision of the weak coupling constant, i.e., $[\ln(\Delta/\omega_D)]^{-1} \sim 0.3$. For the case of the two-band model such a crude estimate can be checked more accurately by direct solution of the nonlinear matrix equation for the energy gap. It has following form:

$$\Delta_i = \sum_j V_{ij} c_j \Delta_j \left[\frac{1}{\lambda_+} - f(\beta \Delta_j) \right], \tag{16}$$

where i, j take values σ, π and $f(x)=\int_{-\infty}^{\infty}(\tanh u/u - \tanh\sqrt{u^2+x^2}/\sqrt{u^2+x^2})du$. Its solution can be found as a superposition of two normalized eigenstates of the corresponding linear equation: $\Delta_j = Q_+ \Psi_{+j} + Q_- \Psi_{-j}$. In our calculations we used only one of them, Ψ_+ corresponding to the larger eigenvalue λ_+. Such an approximation is justified when the second eigenvalue λ_- is much less than λ_+, even if λ_+ is not very small. Indeed, the symmetrized matrix $\tilde{V}$ with matrix elements $\tilde{V}_{ij} = \sqrt{c_i c_j} V_{ij}$ can be represented as $\tilde{V} = \lambda_+ |+\rangle\langle+| + \lambda_- |-\rangle\langle-|$. This representation shows that at $\lambda_- = 0$ the operator $\tilde{V}$ is separable, and the solution of nonlinear equation (16) is factorizable: $\Delta = Q(T)\Psi_+$. The equation $\lambda_- = 0$ is equivalent to $\mathrm{Det}\, V = V_{\sigma\sigma} V_{\pi\pi} - V_{\pi\sigma}^2 = 0$. Though such a fine tuning of parameters seems improbable, our numerical calculations demonstrate that the ratio λ_-/λ_+ and the thermal variation of the ratio Δ_π/Δ_σ remain small (about 3%) even at $\mathrm{Det}\, V/(c_\sigma V_{\sigma\sigma} + c_\pi V_{\pi\pi})^2 \sim \pm 0.2$. Thus the experimental facts seem to indicate that one of the two eigenvalues is significantly smaller than the other. Such a situation occurred earlier in a band calculation for high-T_c superconductors.[27,28]

The second aspect mentioned in the preamble is that the BCS approximation itself has a low precision and should be substituted by the Eliashberg formalism. The numerical calculations by Golubov *et al.*[3] indicate that the Eliashberg weight function is very small in a broad range of low energy and has rather sharp peaks in the range of 800–1000 K. This is an unusual situation. Leavens and Carbotte[29] considered an extended Eliashberg weight function $\alpha^2 F(\omega)$ centered at values $\omega \sim \omega_0$ much larger than the superconducting energy gap $\Delta(0)$. They argued on the basis of numerical calculations that in this case the function $\Delta(\omega)$ varies very weakly at $\omega < \omega_0$ and then rapidly changes sign. They even modeled $\Delta(\omega)$ by the step function. Their arguments seem to be cor-

rect for the considered case as well. Then it is obvious that by integrating in the range of high frequency, it is possible to obtain the BCS-like equations with a renormalized, not small interaction between electrons with momenta on the Fermi surface. Though such an explanation is plausible, further study of the Eliashberg equation with a model weight is highly desirable.

When this Brief Report was submitted for print, an article[30] was published in which the authors arrived at a similar conclusion on the *de facto* applicability of the weak-coupling two-band model to MgB_2. A new element in our Brief Report is the analysis of the question why this approximation works.

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[1] R. S. Gonnelli *et al.*, Supercond. Sci. Technol. **16**, 171 (2003).
[2] I. I. Mazin *et al.*, Phys. Rev. Lett. **89**, 107002 (2002).
[3] A. A. Golubov *et al.*, J. Phys.: Condens. Matter **14**, 1353 (2002).
[4] S. V. Shulga *et al.*, cond-mat/0103154.
[5] V. L. Pokrovsky, Zh. Eksp. Teor. Fiz. **40**, 641 (1961) [Sov. Phys. JETP **13**, 447 (1961)].
[6] V. L. Pokrovsky and M. S. Ryvkin, Zh. Eksp. Teor. Fiz. **43**, 92 (1962) [Sov. Phys. JETP **16**, 67 (1963)].
[7] B. T. Geilikman, R. O. Zaitsev, and V. Z. Kresin, Sov. Phys. Solid State **9**, 642 (1967).
[8] P. Hohenberg, Zh. Eksp. Teor. Fiz. **45**, 1208 (1963) [Sov. Phys. JETP **18**, 834 (1964)].
[9] D. Markowitz and L. P. Kadanoff, Phys. Rev. **131**, 363 (1963).
[10] J. R. Clem, Ann. Phys. (N.Y.) **40**, 268 (1966).
[11] N. V. Zavaritskii, Sov. Phys. JETP **34**, 1116 (1958).
[12] K. D. Belashchenko, M. van Schilfgaarde, and V. P. Antropov, Phys. Rev. B **64**, 092503 (2001).
[13] H. J. Choi, D. Roundy, H. Sun, M. L. Cohen, and S. G. Louie, Nature (London) **418**, 758 (2002).
[14] V. A. Moskalenko, Fiz. Met. Metalloved. **8**, 503 (1959) [Phys. Met. Metallogr. **8**, 25 (1959)].
[15] H. Suhl, B. T. Matthias, and L. R. Walker, Phys. Rev. Lett. **3**, 552 (1959).
[16] A. Y. Liu, I. I. Mazin, and J. Kortus, Phys. Rev. Lett. **87**, 087005 (2001).
[17] V. G. Kogan, Phys. Rev. B **66**, 020509(R) (2002).
[18] T. M. Mishonov *et al.*, cond-mat/0212491.
[19] T. Mishonov and E. Penev, Int. J. Mod. Phys. B **16**, 3573 (2002); T. Mishonov, S.-L. Drechsler, and E. Penev, Mod. Phys. Lett. B **17**, 755 (2003).
[20] F. Bouquet, Y. Wang, I. Sheikin, P. Toulemonde, M. Eisterer, H. W. Weber, S. Lee, S. Tajima, and A. Junod, Physica C **385**, 192 (2003).
[21] R. S Gonnelli *et al.*, Phys. Rev. Lett. **89**, 247004 (2002).
[22] L. Lyard *et al.*, Phys. Rev. B **66**, 180502(R) (2002).
[23] P. Miranović, K. Machida, and V. G. Kogan, J. Phys. Soc. Jpn. **72**, 221 (2003).
[24] T. Dahm and N. Schopohl, Phys. Rev. Lett. **91**, 017001 (2003).
[25] E. Helfand and N. R. Werthamer, Phys. Rev. **147**, 288 (1966).
[26] S. V. Pokrovsky and V. L. Pokrovsky, Phys. Rev. B **54**, 13 275 (1996).
[27] T. M. Mishonov, E. S. Penev, J. O. Indekeu, and V. L. Pokrovsky, Phys. Rev. B **68**, 104517 (2003).
[28] T. M. Mishonov, J. O. Indekeu, and E. S. Penev, J. Phys.: Condens. Matter **15**, 4429 (2003).
[29] C. R. Leavens and J. P. Carbotte, Can. J. Phys. **49**, 724 (1971); see also the review J. P. Carbotte, Rev. Mod. Phys. **62**, 1027 (1990).
[30] M. E. Zhitomirsky and V.-H. Dao, Phys. Rev. B **69**, 054508 (2004).