

Superconducting transition temperatures of the elements related to elastic constants

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Received 11 February 2004 / Received in final form 13 May 2004

Published online 23 July 2004 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2004

Abstract. For a given crystal structure, say body-centred-cubic, the many-body Hamiltonian H in which nuclear and electron motions are to be treated from the outset on the same footing, has parameters, for the elements, which can be classified as (i) atomic mass M , (ii) atomic number Z , characterizing the external potential in which electrons move, and (iii) bcc lattice spacing, or equivalently one can utilize atomic volume, Ω . Since the thermodynamic quantities can be determined from H , we conclude that T_c , the superconducting transition temperature, when it is non-zero, may be formally expressed as $T_c = T_c^{(M)}(Z, \Omega)$. One piece of evidence in support is that, in an atomic number vs. atomic volume graph, the superconducting elements lie in a well defined region. Two other relevant points are that (a) T_c is related by BCS theory, though not simply, to the Debye temperature, which in turn is calculable from the elastic constants C_{11} , C_{12} , and C_{44} , the atomic weight and the atomic volume, and (b) T_c for five bcc transition metals is linear in the Cauchy deviation $C^* = (C_{12} - C_{44})/(C_{12} + C_{44})$. Finally, via elastic constants, mass density and atomic volume, a correlation between C^* and the Debye temperature is established for the five bcc transition elements.

PACS. 74.62.-c Transition temperature variations – 74.70.Ad Metals; alloys and binary compounds

1 Background and outline

We have recently been concerned with both empirical and theoretical relations between the superconducting transition temperature T_c of high- T_c cuprates and of heavy Fermion materials [1–3]. The generally complex crystallographic structure of such compounds makes it difficult to identify useful correlations between their superconducting properties (such as T_c) and the elastic properties of the lattice. This is not the case of several superconducting elements with a definite and relatively simple crystallographic structure, e.g. characterized by only a few non-zero components of the elastic tensor. Although any such correlation applying to the ‘simple’ superconducting elements may not be immediately generalized to other unconventional superconductors, they are anyway expected to focus on the relevant variables which would be worthwhile studying, both experimentally and theoretically, also in the new classes of superconductors.

Following the Bardeen-Cooper-Schrieffer (BCS) theory [4] of the metallic elements, firmly rooted in electron-phonon interaction as the basic mechanism resulting in

the formation of Cooper pairs, questions have come up regarding the role of strong electron-electron interactions in both the high- T_c cuprates and heavy Fermion systems.

Here, our basic philosophy will be to insist that if we were able to solve the many-body Schrödinger equation for the (considered infinite) superconducting materials, then by treating the motion of nuclei and electrons on the same footing, plus full inclusion of electron-electron interactions, such uncertainties involved in separating electron-lattice and Coulomb repulsions between electrons would be bypassed.

Having said that, let us take as the simplest starting point the metallic elements. Then, the input information into any computer programme to treat these elements would be as follows. First, of course, we should need to specify the structure. To be definite, below we shall single out the body-centred cubic (bcc) lattice, but everything that follows would be equally applicable to the more closely packed face-centred cubic (fcc) structure. Once the structure is specified, one would need to insert the atomic volume Ω (or, of course, essentially equivalently, the lattice parameter a). Then, the external potential created by the nuclei must be specified, which requires the atomic

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number Z as further input. Since one has a many-body Hamiltonian containing both electron and nuclear kinetic energies, one needs also the nuclear mass M . Of course, we take as obvious the input additionally of the fundamental constants h and e , plus the electronic mass m .

The conclusion from the many-body Hamiltonian is therefore that, for a specified structure which we take to be bcc for reasons that will emerge below, the superconducting transition temperature T_c , given from the many-body partition function once the Schrödinger equation has been solved depends, apart from the given fundamental constants h , e and m , on M , Z and Ω , that is

$$T_c = T_c^{(M)}(Z, \Omega). \quad (1)$$

Of course, for all other classes of superconductors than the metallic elements we have more than one atomic number, possibly the next simplest case being the alkali-doped fullerenes (see some brief comments in Sect. 5).

With this as background, the outline of the paper is as follows. Section 2 picks out specifically five bcc superconducting transition elements, W, Mo, Ta, V and Nb. Two more elements, Cr and Fe, have low temperature bcc structures but exhibit cooperative magnetism at low temperatures (antiferro- and ferro-magnetism, respectively) and are not superconductors at the lowest temperature they have yet been subjected to. The five elements listed above are considered in the (Ω, Z) plane with respect to their transition temperatures, the reduced isotope effects being taken as evidence that in equation (1) there is, at most, a weak and therefore relatively unimportant dependence of T_c on nuclear isotopic mass. Since even then $T_c = T_c^{(M)}(Z, \Omega)$ presents problems in its representation, Section 3 reintroduces a classification of the above five elements in which T_c is related to the Cauchy discrepancy, i.e. the departure of C_{12} from C_{44} , where these are two of the three elastic constants (C_{11} being the other) required to characterize a cubic crystal. Section 4 then returns to an essential ingredient of BCS theory, and by using a semiempirical approach throws light on the way the Cauchy deviation relates to the Debye temperature. Section 5 constitutes a summary, plus some proposals for further studies, both theoretical and experimental, which should prove fruitful. An appendix considers zero temperature properties, and in particular critical field $H_c(0)$ and energy gap $E_g(0)$, as functions of the Cauchy discrepancy.

2 Dependence of T_c on atomic number Z and atomic volume Ω in bcc transition elements

In Figure 1, a plot is made of the positions of the five elements in the (Ω, Z) plane, the values of T_c being attached to these coordinates.

That both Ω and Z are important variables in characterizing T_c is immediately apparent. As to the functional form $T_c(\Omega, Z)$, one can comment that: (i) For constant atomic volume, T_c markedly decreases with increasing atomic number. (ii) For constant Z , there is plainly

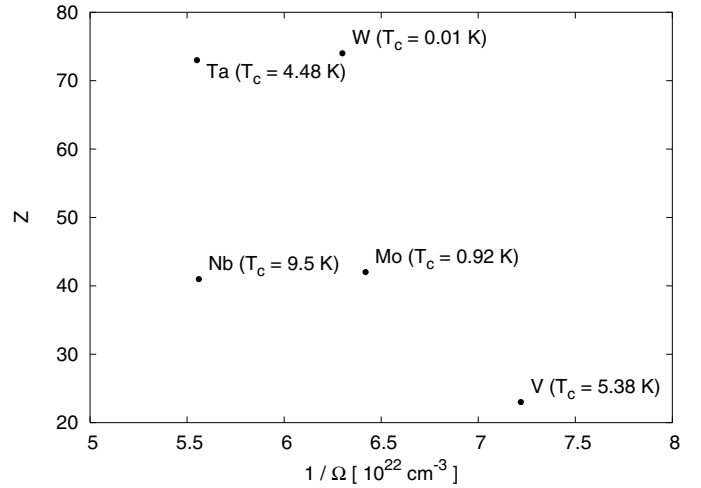


Fig. 1. Shows five superconducting bcc transition elements in the (Ω, Z) plane. Actual abscissa is the reciprocal of the atomic volume, Ω^{-1} . To each point, the value of the critical temperature T_c is attached.

Table 1. Pressure derivatives of T_c [5], experimental bulk moduli [6], and inferred partial derivatives of T_c with respect to Ω at constant Z , equation (2), of the bcc superconducting transition metals at $P = 0$.

Element	W	Mo	Ta	V	Nb
$\frac{\partial T_c}{\partial P}$ [K/GPa]	—	-1.4	-2.6	6.3	-2.0
B [GPa]	323	272	200	162	170
$\frac{\partial T_c}{\partial \Omega}$ [10^{31} K m $^{-3}$]	—	2.4	2.9	-7.4	1.9

substantial variation of T_c with atomic volume, which is proportional to the reciprocal of the concentration. Relevant to such variation is the pressure dependence of T_c for a given element, provided one remains within the bcc phase.

Despite high pressure can turn many elements into superconductors via an insulator-metal transition, T_c usually decreases with increasing pressure for most superconducting elements at ambient pressure (see Tab. 1). Within BCS theory [see also Eq. (5) below] or its extension by McMillan, this is usually justified in terms of a pressure-induced lattice stiffening, which reduces the electron-phonon constant at a more rapid rate than the electron density of states at the Fermi level is increased [7]. Pressure derivatives of T_c can then be straightforwardly related to volume derivatives (at constant Z) from the relation

$$\frac{\partial \log T_c}{\partial \log \Omega} = -B \frac{\partial \log T_c}{\partial P}, \quad (2)$$

where B is the bulk modulus (see Tab. 1).

However, even given some knowledge of these partial derivatives, the fact that T_c depends apparently in a sensitive way on these two variables for the chosen bcc structure leaves open the detailed form of the function $T_c(\Omega, Z)$ for this structure. Therefore in the following section we appeal to a known, but so far rather neglected, correlation between T_c and the Cauchy discrepancy $C_{12} - C_{44}$ between elastic constants. This is important for our present study, since it is clear that T_c can, in fact, be characterized by a single variable, rather than the pair (Ω, Z) used in Figure 1.

3 Characterization of T_c by the Cauchy discrepancy for the five bcc transition elements

Figure 2, redrawn from the work of Ledbetter [8] carried out almost a quarter of a century ago, shows a plot of T_c versus the quantity C^* defined by

$$C^* = \frac{C_{12} - C_{44}}{C_{12} + C_{44}}. \quad (3)$$

Ledbetter [8] also included some alloys, namely $\text{Nb}_{0.9}\text{Zr}_{0.1}$, $\text{Nb}_{0.4}\text{Ti}_{0.6}$, and $\text{Ti}_{0.7}\text{V}_{0.3}$, but we have omitted these from the redrawn Figure 2, even though the alloys support the general trend of the correlation shown. Also, the points for the bcc elements Cr and Fe have been omitted, since these elements are both characterized by magnetic order and no superconductivity in normal conditions. It should be mentioned, however, that a high-pressure, non-magnetic, but also a non-bcc phase of iron has been recently reported to display superconductivity with $T_c < 2$ K between 15 and 30 GPa [9].

The equation of the straight line drawn in Figure 2 is

$$T_c [\text{K}] = AC^* - B, \quad (4)$$

with $A = 17.7$ K and $B = 1.65$ K. Though presently we do not have theory to allow the evaluation of A and B from first principles, the correlation in equation (4) leads us, in the following section, to attempt to relate C^* to a basic ingredient of BCS theory, the Debye temperature Θ_D .

4 Cauchy discrepancy related to Θ_D , which gives the ‘scale’ of T_c in the BCS theory

As Allen and Mitrovic [10] have stressed, notwithstanding the numerous impressive and successful predictions for the metallic elements of BCS theory, their formula (see Ref. [10], Eq. (2.29))

$$T_c = 1.13\Theta_D \exp\left(-\frac{1}{N(E_F)V}\right), \quad (5)$$

where $N(E_F)$ is the density of states at the Fermi level and V is the electron-phonon coupling constant, is not a

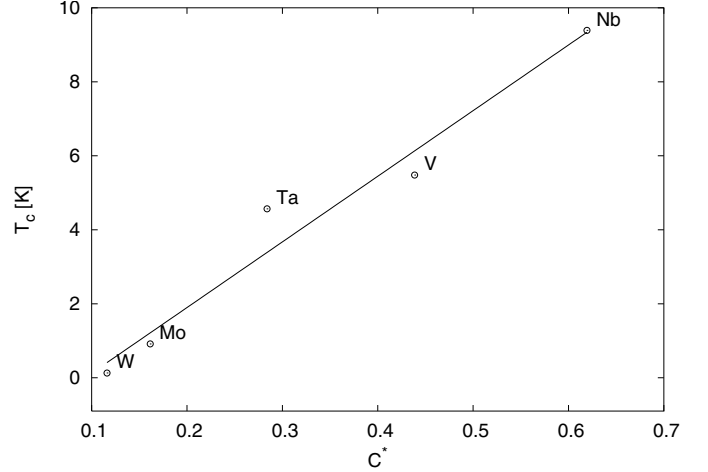


Fig. 2. Superconducting critical temperatures for bcc transition elements correlated with Cauchy discrepancy, equation (3). Solid line is best fit to the points [see text for discussion, in particular Eq. (4)]. Redrawn from reference [8] (see also [6] for an update on elastic constants data).

successful way of correlating values of T_c for the metallic elements. Nevertheless, it suggests that one should re-open empirically the question of a correlation between T_c and Θ_D . Therefore, more generally than for the bcc transition metals, we have redrawn data by de Launay and Dolecek [11] in Figure 3 (top panel), adding values for W and Mo.

While, for mainly non-transition elements, the continuous line drawn in Figure 3 (top panel), already given by de Launay and Dolecek [11] a decade before BCS theory, shows a relation between T_c and Θ_D , it is far from simple. And the triangle involving Ta, V and Nb modified from the 1947 figure of de Launay and Dolecek [11] shows no relation to the continuous curve.

Nevertheless, Θ_D lies deeply enough in first principles theory to enquire whether it can be connected, albeit not simply, with the Cauchy deviation C^* , which is much more directly related to T_c , as shown in the previous section.

To attempt this, we note that numerous earlier workers have calculated the Debye temperature for cubic crystals from knowledge of the elastic constants C_{11} , C_{12} and C_{44} , the mass density and the atomic volume Ω . While Houston’s method [12] is favoured, and has been developed by Betts et al. [13,14], we have found the semi-empirical relation of Blackman [15], quoted in Huntington’s review article [16], a useful starting point. This reads

$$\Theta_D^3 = \frac{3.15}{8\pi} \left(\frac{h}{k_B}\right)^3 \frac{s}{\rho^{\frac{3}{2}}\Omega} \times (C_{11} - C_{12})^{\frac{1}{2}} (C_{11} + C_{12} + 2C_{44})^{\frac{1}{2}} C_{44}^{\frac{1}{2}}, \quad (6)$$

where s is the number of atoms in the unit cell and ρ is the mass density. This approximate result, equation (6),

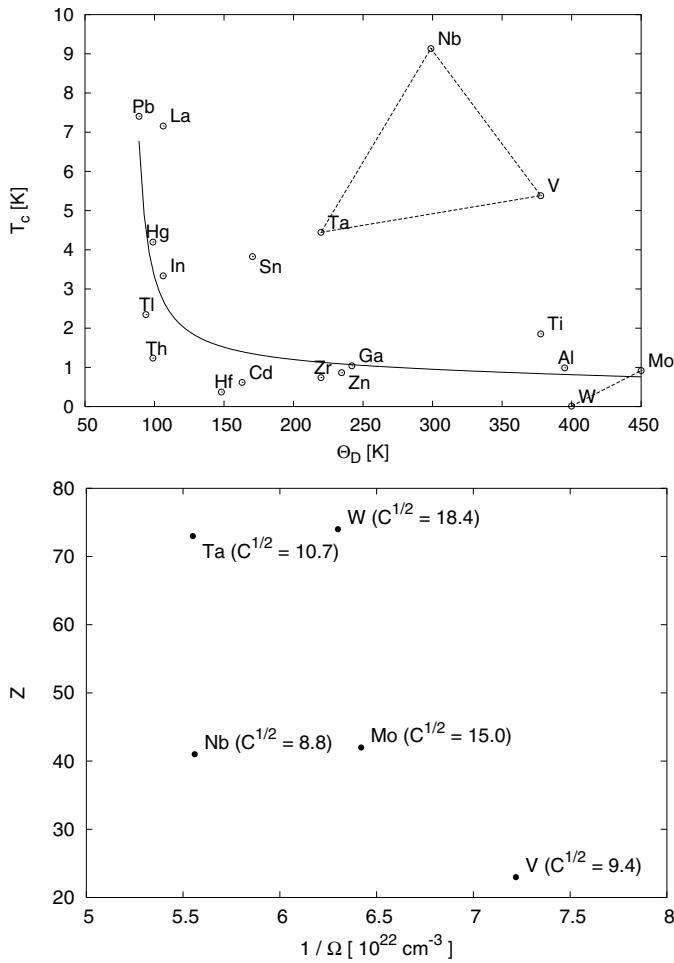


Fig. 3. *Top:* Superconducting transition temperatures versus Debye temperatures for numerous elements. Redrawn after reference [11]. Solid and dashed lines are guides to the eye. See text for discussion. *Bottom:* Same as Figure 1, but now with attached values of square root $C^{1/2}$ of the ‘average’ elastic constant, as defined by equation (7), in $\text{GPa}^{1/2}$.

motivates the definition of an ‘average’ elastic constant

$$C = \left(\frac{8\pi}{3.15} \right)^{2/3} \left(\frac{k_B}{h} \right)^2 \frac{\rho \Omega^{2/3}}{s^{2/3}} \Theta_D^2, \quad (7)$$

and Figure 3 (bottom panel) parallels Figure 1 except that coordinates in the (Ω, Z) plane are now labelled by $C^{1/2}$. Evidently from this figure at constant volume Ω , $C^{1/2}$ related to Θ_D through equation (7) increases with increasing Z , in contrast to the behaviour of T_c in Figure 1. Also at constant Z , $C^{1/2}$ increases with decreasing atomic volume. Nevertheless, again prompted by the BCS theory, we have sought to correlate $C^{1/2}$ with T_c , but now via the Cauchy discrepancy. Figure 4 shows, for the five bcc elements, that there is indeed a marked correlation, the functional form obtained empirically being recorded in the caption.

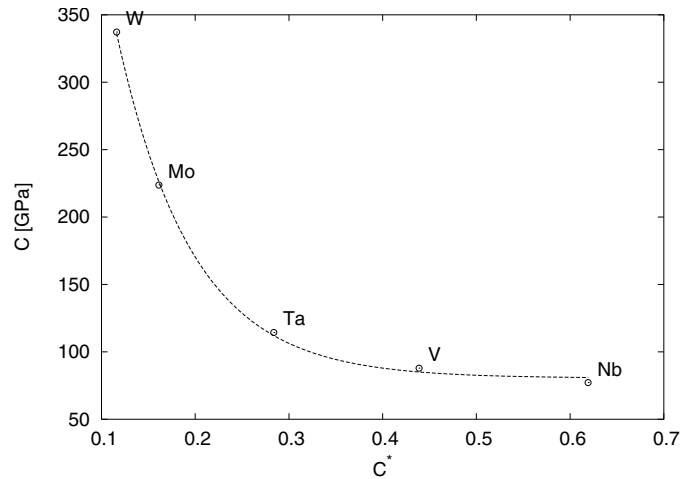


Fig. 4. Shows ‘average’ elastic constant C , equation (7), as a function of Cauchy discrepancy C^* , equation (3), for the five bcc transition metals. Dashed line is a guide for the eye, which actually employs an exponential functional form, of the kind $C = \alpha + \beta \exp(-\gamma C^*)$, with $\alpha = 80.5$ GPa, $\beta = 1008.9$ GPa, $\gamma = 12.5$.

5 Summary and directions for future work

Though the top panel of Figure 3 makes it quite clear that there is no simple relation between Debye temperature Θ_D and the superconducting temperature T_c , we have been led, via the considerations from Figures 1 and 3 (lower panel), to attempt to correlate C , having dimensions of an elastic constant and defined in equation (7), which in turn involved Θ_D , with the Cauchy discrepancy C^* in equation (3). These quantities, for the five bcc elements we have focussed on here, are clearly inter-related, as Figure 4 demonstrates, and the functional form has been extracted. Since, as Ledbetter [8] already pointed out in 1980, T_c relates linearly to C^* as in Figure 2, there is a clear correlation between T_c and Θ_D , with mass density and atomic volume entering through the definition of the ‘average’ elastic constant in equation (7). Furthermore, and again motivated by BCS theory, zero temperature quantities, namely critical field $H_c(0)$ and energy gap $E_g(0)$ are shown also to correlate simply with the Cauchy discrepancy C^* for the five bcc superconducting transition elements in Figures 5 and 6.

The present work stimulates thoughts concerning generalization of the basic approach set out here to other groups of superconductors. Our view is that the next simplest class to study is the alkali-doped C_{60} compounds, the fullerides, which have been reviewed by Gunnarsson [17]. In Figure 3 of this review, Gunnarsson has plotted T_c for Rb_3C_{60} and K_3C_{60} , as a function of lattice parameter, which was varied by applying pressure, P . There is a remarkably linear increase in T_c with P . For $\text{Na}_2\text{Rb}_x\text{Cs}_{1-x}\text{C}_{60}$ there is again a linear variation of T_c with lattice parameter, but with a much steeper slope. It will be of interest for the future to attempt a generalization of the approach given here for the metallic elements

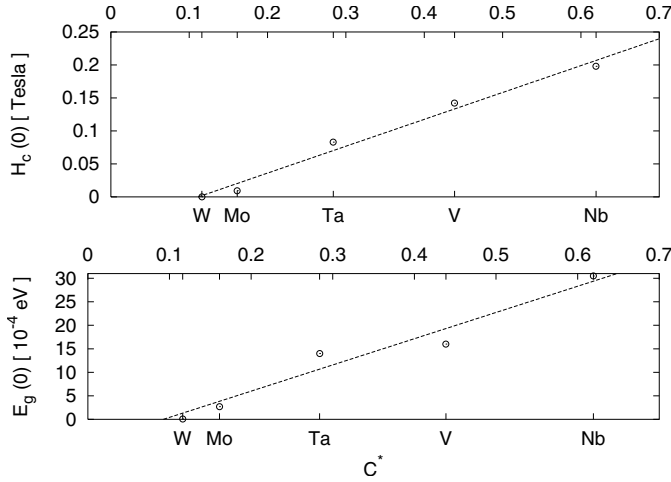


Fig. 5. Experimental results for critical field $H_c(0)$ and energy gap $E_g(0)$, as extracted from tunnelling measurements, vs. Cauchy discrepancy C^* , as defined in equation (3).

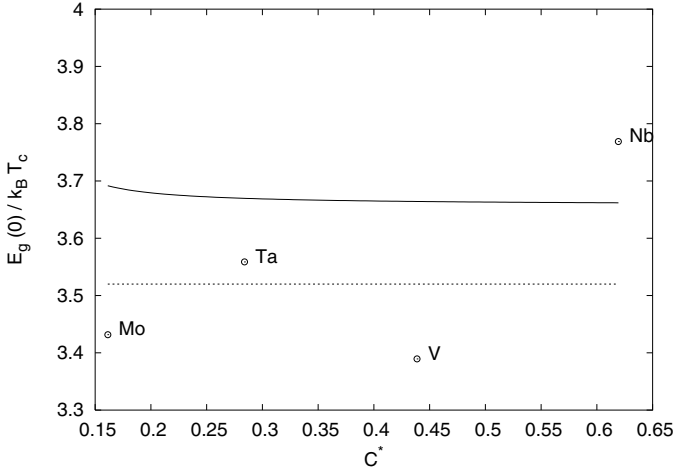


Fig. 6. BCS ratio $E_g(0)/k_B T_c$ for bcc transition elements. Solid line is ratio of equations (4) and (9), while dashed line is BCS theoretical value.

to the fullerenes, in view of these striking correlations between T_c and lattice parameter.

G.G.N.A. thanks the Department of Physics, University of Antwerp, for much hospitality.

Appendix A: Zero temperature properties, related by BCS theory to T_c , as functions of Cauchy discrepancy C^*

The purpose of this appendix is to display a marked correlation between experimentally estimated values of the critical field $H_c(0)$ and the energy $E_g(0)$, as extracted from tunnelling experiments, and the Cauchy discrepancy C^* , equation (3). Thus, the upper panel of Figure 5 shows $H_c(0)$ plotted against C^* for the five bcc transition elements on which attention was focussed in the body of the

text. The data for $H_c(0)$ have been taken from Kittel's book [18] (see also [19]). Evidently, as for T_c in Figure 2, a marked correlation again exists, the dashed line having the equation

$$H_c(0) = b_1 C^* - b_2, \quad (8)$$

with $b_1 = 0.41$ tesla and $b_2 = 0.05$ tesla.

The energy gap $E_g(0)$, as estimated from tunnelling experiments, has again been taken from data given by Kittel [18] (see also [5]), and is shown in the lower panel of Figure 5 for the same set of bcc transition elements. The dashed line, but now with more substantial scatter of the experimental points than for either T_c or $H_c(0)$, has the equation

$$E_g(0) = e_1 C^* - e_2, \quad (9)$$

with $e_1 = 55.8 \times 10^{-4}$ eV and $e_2 = 5.16 \times 10^{-4}$ eV.

BCS theory predicts a constant value for the ratio $E_g(0)/k_B T_c$. Since equations (4) and (9), respectively, give a reasonable overall fit for the five bcc transition elements focussed on in the present study, we have finally plotted the 'average' ratio $E_g(0)/k_B T_c$ from equations (4) and (9) as a function of C^* in Figure 6 using the given parameters A , B , e_1 and e_2 .

References

1. G.G.N. Angilella, N.H. March, R. Pucci, Phys. Rev. B **62**, 13919 (2000)
2. G.G.N. Angilella, N.H. March, R. Pucci, Phys. Rev. B **65**, 092509 (2002)
3. G.G.N. Angilella, F.E. Leys, N.H. March, R. Pucci, Phys. Lett. A **322**, 475 (2004)
4. J.R. Schrieffer, *Theory of Superconductivity* (W.A. Benjamin, New York, 1964)
5. Ch.P. Poole, H.A. Farach, R.J. Creswick, *Superconductivity* (Academic Press, San Diego, 1995)
6. M.J. Mehl, D.A. Papaconstantopoulos, Phys. Rev. B **54**, 4519 (1996)
7. J.S. Schilling, in *Frontiers of high pressure research II: Application of high pressure to low-dimensional novel electronic materials*, Vol. 48 of *NATO Science Series*, edited by H.D. Hochheimer, B. Kuchta, P.K. Dorhout, J.L. Yarger (Kluwer, Dordrecht, 2001)
8. H.M. Ledbetter, Phys. Lett. A **77**, 359 (1980)
9. K. Shimizu, T. Kimura, S. Furomoto, K. Takeda, K. Kontani, Y. Onuki, K. Amaya, Nature **412**, 316 (2001)
10. P.B. Allen, B. Mitrovic, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, D. Turnbull (Academic Press, New York, 1982), Vol. 37
11. J. de Launay, R.L. Dolecek, Phys. Rev. **72**, 141 (1947)
12. W.V. Houston, Rev. Mod. Phys. **20**, 164 (1948)
13. D.D. Betts, A.B. Bhatia, M. Wyman, Phys. Rev. **104**, 37 (1956)
14. D.D. Betts, A.B. Bhatia, G.K. Horton, Phys. Rev. **104**, 43 (1956)
15. M. Blackman, Phil. Mag. **42**, 1441 (1951)
16. H.B. Huntington, in *Solid State Physics*, edited by F. Seitz, D. Turnbull (Academic Press, New York, 1958), Vol. 7
17. O. Gunnarsson, Rev. Mod. Phys. **69**, 575 (1997)
18. C. Kittel, *Introduction to Solid State Physics* (J. Wiley and Sons, New York, 1996)
19. H.P. Myers, *Introductory Solid State Physics* (Taylor and Francis, London, 1997)