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2008 J. Phys.: Condens. Matter 20 434226

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# Critical temperature and the giant isotope effect in the presence of paramagnons

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Received 7 July 2008

Published 9 October 2008

Online at [stacks.iop.org/JPhysCM/20/434226](http://stacks.iop.org/JPhysCM/20/434226)

## Abstract

We reconsider the long-standing problem of the effect of spin fluctuations on the critical temperature and the isotope effect in a phonon-mediated superconductor. We discuss the general physics of the interplay between phonons and paramagnons, and show that the previously used approximate formulas fail to describe the correct behavior of  $T_c$  for general phonon and paramagnon spectra. Using a controllable approximation, we derive an analytical formula for  $T_c$  which agrees well with exact numerical solutions of the Eliashberg equations for a broad range of parameters. On the basis of both numerical and analytical results, we predict a strong enhancement of the isotope effect when the frequencies of spin fluctuation and phonons are of the same order. We discuss application to near-magnetic superconductors such as MgCNi<sub>3</sub>.

(Some figures in this article are in colour only in the electronic version)

In the last decade a large number of superconductors have been discovered in which enhanced spin fluctuations (SF) play a role in the superconductivity, e.g., Sr<sub>2</sub>RuO<sub>4</sub>, MgCNi<sub>3</sub>, ε-Fe, ZrZn<sub>2</sub>, and others, introducing new and interesting physics. However, understanding such materials, even at an intuitive level, has been hindered by the lack of a simple formula that would approximate the full Eliashberg theory in a compact analytical form, as the conventional McMillan formula (MMF) does. As a result, uncritical generalizations of the latter have been used as a substitute, despite the fact that, as we will show below, some of them are too approximate or actually outright incorrect. In this paper we present an analogue of the MMF, derived in a controllable way and tested against numerical solutions of full Eliashberg equations, including interaction with SF (paramagnons). We point out the possibility of a giant *phonon* isotope effect induced by SF. We will also apply this theory, as an example, to a nearly ferromagnetic superconductor, MgCNi<sub>3</sub>.

The understanding that SF are pair breakers in conventional superconductors is nearly as old as the BCS theory itself [1]. Moreover, it was soon realized that strong coupling manifests itself in a nontrivial way in the presence of SF [2, 3]. In a number of papers, numerical solutions of the Eliashberg equations were presented, incorporating phonon ( $\alpha^2 F_p(\omega)$ ) as

well as SF ( $\alpha^2 F_s(\omega)$ ) spectral functions (see, e.g., [4]). However, solving the full Eliashberg equation is not always an option, and does not provide as much physical insight as analytical treatment. An analytical tool comparable to the famed MMF is needed.

Retrospectively, one can realize that the overwhelming success of the MMF is due to three factors: (a) it can be derived analytically using simple approximations, (b) it includes Coulomb repulsion effects, (c) it has three universal adjustable parameters, which, after little tuning, produce an expression which is surprisingly accurate for a large range of phonon frequencies and coupling strengths. Compared to the BCS equation, the MMF includes three essential pieces of additional physics: effective mass renormalization, logarithmic reduction of the Coulomb repulsion, and proper (logarithmic) averaging of the phonon frequency. All three effects can be derived analytically in some approximations. In fact, it is known that the functional form of the MMF can be derived in two different ways. One, known as the square-well model [5], uses the Matsubara representation, where the coupling with the phonons is parameterized in terms of the matrix  $\lambda(n, n')$ . The model assumes two different approximations for the same function  $\lambda(n, n')$ , depending on whether it is used in the

equation for the mass renormalization  $Z$  or in the one for the gap function  $\phi$ :

$$\begin{aligned}\lambda_Z(n, n') &= \lambda_p \Theta(\omega_p - |\omega_{n-n'}|) \\ \lambda_\phi(n, n') &= \lambda_p \Theta(\omega_p - |\omega_n|) \Theta(\omega_p - |\omega_{n'}|).\end{aligned}\quad (1)$$

This models leads to an equation for the critical temperature,  $T_c$ ,

$$T_c = a\omega_{\log} \exp\{-b(1 + \lambda_Z)/[\lambda_\phi - \mu^*(1 + c\lambda_Z)],\quad (2)$$

where the theoretical parameters are  $a = 1.14$ ,  $b = c = 1$ ,  $\lambda_Z = \lambda_\phi = \lambda_p = 2 \int_0^\infty \omega^{-1} \alpha^2 F_p(\omega) d\omega$  and  $\lambda_p \ln \omega_{\log} = 2 \int_0^\infty \omega^{-1} \ln \omega \alpha^2 F_p(\omega) d\omega$ . The renormalized Coulomb potential is reduced from its bare value  $\mu$  as  $\mu^* = \mu/(1 + \mu \ln \frac{\omega_C}{\omega_{\log}})$ , where  $\omega_C$  characterizes the frequency cutoff of the Coulomb interaction. The MMF formula is given by equation (2) with optimized parameters  $a = 1/1.2$ ,  $b = 1.04$ , and  $c = 0.62$ .

SF, as opposed to phonons, induce repulsion for singlet pairs. However, they contribute to the mass renormalization just the same. Therefore the first instinctive notion is to let  $\lambda_Z = \lambda_p + \lambda_s$ , where  $\lambda_s$  describes the SF, and  $\lambda_\phi = \lambda_p - \lambda_s$ . Equation (2) with this modification and standard  $a$ ,  $b$  and  $c$  is the one routinely used in the literature for materials with SF (e.g., [6–8]).

Obviously, using two different approximations for the same physical function  $\lambda(n, n')$  depending on whether it appears in the first or second Eliashberg equation cannot be justified by any logic. It *appears* that the MMF formula can be *fortuitously* derived in this way, but, as we will see below, this approach fails when SF are included. An alternative derivation of the MMF utilizes the real frequency axis formalism [9]. The one-mode approximation is used, which assumes an Einstein phonon at a frequency  $\omega_p$ , i.e.,  $\alpha^2 F(\omega) = \lambda_p \omega_p \delta(\omega - \omega_p)/2$ . The Eliashberg equations are then solved iteratively. After the first iteration one obtains [9]

$$T_c = 1.14\omega_p \exp\left\{-\frac{1}{2} - \frac{1 + \lambda_p}{\lambda_p - \mu^*[1 + 0.5 \frac{\lambda_p}{1 + \lambda_p}]}\right\}, \quad (3)$$

which is similar to the square-well formula equation (2) with  $a = 1.14/\sqrt{e} = 1/1.44$  (note that this value of  $a$  is much closer to the optimized one),  $b = 1$ , and  $c = 0.5/(1 + \lambda_p)$ . This approach is a controllable approximation with a concrete physical meaning. However, it has never been applied to superconductors with SF.

In contrast, several attempts to apply the square-well model to SF have been reported. In [3, 4] the following expression was derived (for  $\mu^* = 0$ ):

$$T_c = 1.14\omega_p^v \omega_s^{1-v} \exp\{-(1 + \lambda_p + \lambda_s)/(\lambda_p - \lambda_s)\}, \quad (4a)$$

$$\text{with } v = \lambda_p/(\lambda_p - \lambda_s)$$

$$\text{or } v = \frac{\lambda_p^2}{\lambda_p - \lambda_s} \left[ \lambda_p - \lambda_s + \frac{\lambda_p \lambda_s}{1 + \lambda_p + \lambda_s} \ln \frac{\omega_p}{\omega_s} \right]^{-1} \quad (4b)$$

where the choice (4a) is due to Carbotte *et al* [4], and (4b) to Vonsovsky *et al* [3]. Unfortunately, neither authors give details of their derivations, so we do not know what was different

in their models. We were not able to reproduce either result. The latest paper utilizing the square-well model (in the weak coupling limit) is that by Shimahara [10]. Our own result for the square-well model reduces to that of [10] in the weak limit, and reads

$$T_c = 1.14\omega_p \exp\left[-\frac{1 + \lambda_s + \lambda_p}{\lambda_p - \frac{\lambda_s(1 + \lambda_s)}{1 + \lambda_s + \lambda_s \ln \frac{\omega_s}{\omega_p}}}\right], \quad \omega_s \geq \omega_p \quad (5)$$

$$T_c = 1.14\omega_s \exp\left[-\frac{1 + \lambda_s + \lambda_p}{\frac{\lambda_p(1 + \lambda_p)}{1 + \lambda_p - \lambda_p \ln \frac{\omega_p}{\omega_s}} - \lambda_s}\right], \quad \omega_s \leq \omega_p. \quad (6)$$

Unlike equation (4), equations (5) and (6) reduce to the McMillan form upon making the substitution  $\omega_s \rightarrow \omega_C \gg \omega_p$ ,  $\lambda_s \rightarrow \mu$ , as they should.

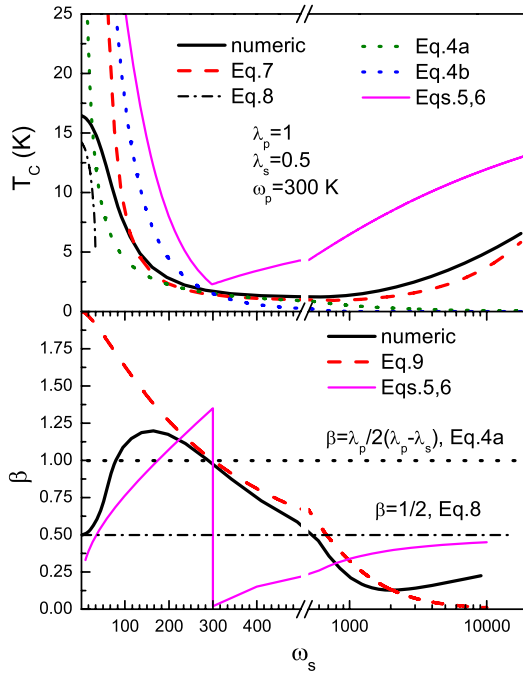
Given the controversy about the square-well model, it is desirable to have a derivation in a controllable approximation, such as the real frequency axis formalism of [9]. Assuming an Einstein phonon at a frequency  $\omega_p$  and an ‘Einstein’ paramagnon at  $\omega_s$ ,  $2\alpha^2 F(\omega) = \lambda_p \omega_p \delta(\omega - \omega_p) - \lambda_s \omega_s \delta(\omega - \omega_s)$ , we obtain the following iterative solution of the Eliashberg equations:

$$\begin{aligned}T_c &= 1.14\omega_p^{\frac{\lambda_p}{\lambda_p - \lambda_s}} \omega_s^{-\frac{\lambda_s}{\lambda_p - \lambda_s}} \exp(K) \\ &\times \exp\left\{-\frac{1 + \lambda_p + \lambda_s}{\lambda_p - \lambda_s - \mu^*(1 - K \frac{\lambda_p - \lambda_s}{1 + \lambda_p + \lambda_s})}\right\} \\ K &= -\frac{1}{2} - \frac{\lambda_p \lambda_s}{(\lambda_p - \lambda_s)^2} \left[ 1 + \frac{\omega_p^2 + \omega_s^2}{\omega_p^2 - \omega_s^2} \ln \frac{\omega_s}{\omega_p} \right].\end{aligned}\quad (7)$$

For  $\omega_p \rightarrow \omega_s$ ,  $K = -1/2$ , and at  $\mu^* = 0$ , equation (7) reduces to equation (4) with  $v = \lambda_p/(\lambda_p - \lambda_s)$ .

As usual, the ultimate test for any approximation is numerical calculations. We solved the Eliashberg equations for a variety of the model  $\alpha^2 F(\omega)$  including SF and compare them with the proposed analytical formulas. In figure 1 we show this comparison for the simplest ‘one-mode’ approximation, one phonon and one paramagnon (we have verified that other model spectra lead to similar results). As we can see, while the equation (7), as well as its simplified version equation (4a), describe the numerical results rather well when  $\omega_s$  and  $\omega_p$  are comparable, the latter fails at  $\omega_s \gg \omega_p$ , and both fail at  $\omega_s \ll \omega_p$ . Both effects can be easily understood: equation (4) includes  $\omega_s$  in a negative power in all regimes, thus leading to a total suppression of superconductivity at  $\omega_s \rightarrow \infty$ . In reality, in this limit the negative effect of the SF is renormalized down logarithmically in the same spirit as the Coulomb repulsion.

Equations (7), (4) diverge at  $\omega_s \rightarrow 0$ . This is due to the fact that the derivations above assume that  $\omega_s, \omega_p \gtrsim \pi T_c$ . It is possible to treat this regime separately. If  $\omega_s \ll T_c$ , the SF act as static magnetic defects, and the standard theory of the magnetic pair breaking [11] can be applied. In the Matsubara representation, at  $\omega_s = 0$  one needs only to keep the term with  $n = m$  in  $\lambda_s(\omega_n - \omega_m)$ . Then the equations reduce



**Figure 1.** Comparison of  $T_c$  and the isotope coefficient with the exact numerical calculations.

to the standard form [5, 11] with the pair breaking parameter  $\gamma \equiv (1/2\tau_p)/\pi T_c = \lambda_s$ . In the weak coupling limit,  $T_c$  is

$$T_c = T_{c0} \exp[\psi(1/2) - \psi(1/2 + \gamma)], \quad (8)$$

where  $T_{c0} = T_c(\lambda_s = 0)$ . One important difference exists between pair breaking by SF with  $\omega_s = 0$  and by magnetic impurities: in the former case the pair breaking parameter  $\gamma$  now does not depend on  $T_c$ . This has consequences for the isotope effect, as we will see below.

For small but finite  $\omega_s \ll \pi T_c$  summation of  $\lambda_s(n - m)$  over  $n - m$  provides the expression for the pair breaking rate in equation (8):  $\gamma = \lambda_s \frac{T_c}{2\omega_s} \coth \frac{T_c}{2\omega_s}$ . This result coincides with equation (5.8) of [12] for dynamical pair breaking in anisotropic superconductors if the anisotropy parameter  $g$  (as defined in [12]) is set to  $-1$ . When  $\omega_s$  increases,  $T_c$  drops sharply with a complete loss of superconductivity at  $\omega_s = \omega_s^* = e^{-C} T_{c0}/2\gamma$  (where  $e^C \simeq 1.78$ ). However, the condition  $\omega_s \ll \pi T_c$  used in the derivation of equation (8) is lost well before  $\omega_s^*$  (in fact, at  $\omega_s \simeq \omega_s^*/2$ ).

One can take into account the strong coupling effects in the square-well model, resulting in a renormalization  $\gamma \rightarrow \gamma/(1 + \lambda_p) = \frac{\lambda_s}{1 + \lambda_p} \frac{T_c}{2\omega_s} \coth \frac{T_c}{2\omega_s}$ . As the comparison with numerical calculations shows (figure 1), this approximation underestimates  $T_c$ . However, it illustrates why  $T_c$  flattens out at a finite value smaller than  $T_{c0}$  when  $\omega_s \rightarrow 0$ , instead of rising as equation (7) suggests.

We also show in figure 1 that both equation (4b) and the square-well model, equations (5) and (6), disagree qualitatively with the numerical results over the whole range of  $\omega_s$ .

We will now turn to the isotope effect. Looking at equation (4), one observes that the isotope coefficient,  $\beta = \nu/2 = \lambda_p/2(\lambda_p - \lambda_s) > 0.5$ , is always enhanced compared

to its BCS value and is independent of the SF frequencies. Clearly, this should hold approximately in the range of applicability of this formula,  $\omega_s \simeq \omega_p \gg \pi T_c$ . Indeed, the more accurate equation (7) yields for  $\beta$

$$\beta = 0.5 \frac{\lambda_p}{\lambda_p - \lambda_s} \left[ 1 - \frac{\lambda_s}{\lambda_p - \lambda_s} F \left( \frac{\omega_s^2}{\omega_p^2} \right) \right] \quad (9)$$

$$F(r) = (r^2 - 2r \ln r - 1)/(r - 1)^2.$$

The second term here is the correction to equation (4). It can be of either sign, since with growing  $r$  the  $F(r)$  monotonically grows from  $-1$  to  $1$ , and  $F(1) = 0$ . As discussed, equation (4) itself becomes invalid at  $\omega_s < \pi T_c$ . As  $\omega_s \rightarrow 0$ , according to equation (8),  $\beta = 0.5$  (note that in the case of magnetic impurities  $\beta > 0.5$  due to the dependence of  $\gamma$  on  $T_c$  [5]). Therefore, the isotope effect has to have a maximum at some  $0 < \omega_s < \omega_p$ , and  $\beta_{\max} > \lambda_p/2(\lambda_p - \lambda_s)$ .<sup>5</sup>

This is confirmed by numerical calculations, which show that the maximum isotope effect for given  $\lambda_s, \lambda_p$  is achieved close to  $\omega_s \sim \omega_p$  and is not far from  $\lambda_p/2(\lambda_p - \lambda_s)$ . This is a very important result, and we emphasize it again: *if superconductivity is depressed by spin fluctuations, the total isotope effect increases compared to its BCS value.*

We shall now apply this formalism to a superconductor where  $T_c$  is believed to be substantially suppressed by SF, MgCNi<sub>3</sub> [7, 14, 15], which has attracted substantial interest not because of its relatively modest critical temperature,  $T_c \approx 8$  K, but because of its unusual antiperovskite crystal structure and proximity to ferromagnetic instability. The latter was first pointed out by Rosner *et al* [7], who believed in such strong coupling with SF that they proposed a p-wave superconductivity. Singh and Mazin [14] also came to the conclusion that SF should play a role in superconductivity of MgCNi<sub>3</sub>, but, on the basis of their frozen phonon calculation, they deduced a large electron–phonon coupling constant ( $\lambda_p \gtrsim 1$ ) due to the bond-bending Ni phonons. They reconciled this relatively large  $\lambda_p$  with a modest  $T_c$  within a scenario of s-wave phonon-induced superconductivity depressed by SF. Later this scenario was reinvented by Shan *et al* [15], who proved the s symmetry of the order parameter by means of tunneling experiments. This point has been since confirmed by several groups and seems to be well established.

Singh and Mazin's [14] prediction of the Ni phonon playing the major role in the electron–phonon coupling in MgNiC<sub>3</sub> was based on a limited number of calculations at a high-symmetry point in the Brillouin zone, and therefore was more an educated guess than a quantitative argument. A quantitative analysis was provided by Ignatov *et al* [16], who performed linear response calculations of the phonon frequencies and their coupling with electrons for the whole Brillouin zone. They found a gigantic coupling for the Ni bond-bending modes, and the most strongly coupled modes (the mode considered by Singh and Mazin was not among them) actually unstable. In other words, they found a set of double-well-type instabilities involving mostly Ni atoms.

<sup>5</sup> This is not the only case where electronic interactions can enhance the isotope effect; cf, e.g., [13].

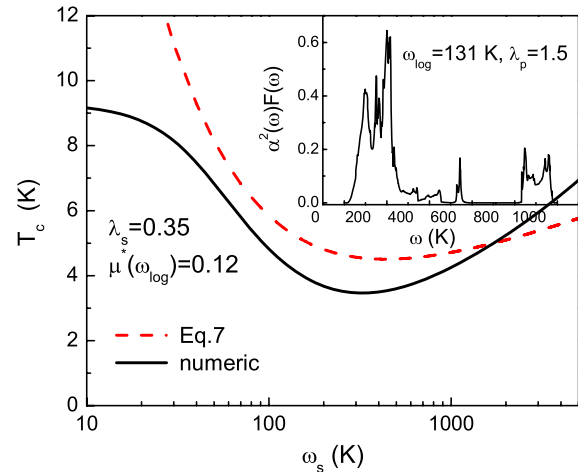
This was verified by means of EXAFS measurements [16]. Ignatov *et al* [16] estimated the total electron–phonon coupling constant as 1.5 and the logarithmically averaged phonon frequency as 131 K.

Thus, the scenario of [14] was modified in [16] in the sense that electron–phonon coupling and superconductivity were coming from highly anharmonic predominantly Ni modes, but not exactly the simple rotations of the Ni<sub>6</sub> octahedra considered in [14]. Unfortunately, strong anharmonicity of these modes makes it impossible to evaluate their coupling with electrons in the linear response calculations, but it is obviously strong. However, one can estimate the electron–phonon and electron–paramagnon coupling indirectly from experimental data. Indeed, specific heat renormalization, from different reports, ranges from 2.6 to 3.1 (see [17] and references therein), implying that the sum  $\lambda_p + \lambda_s$  varies between 1.6 and 2.1. Wälte *et al* [17] estimated  $\omega_p \approx 143$  K, smaller than but comparable to the value calculated in [16],  $\omega_s \approx 25$  K, and the mass renormalization due to paramagnons as  $1 + \lambda_s \approx 1.43$ . Then, using MMF,  $\mu^* = 0.13$ , and  $T_c = 6.8$  K, as measured for their samples, they deduced  $\lambda_p = 1.91$ .

However, there are several problems with this derivation. First of all, as shown above, the proper formula is equation (4). Using this formula instead of equation (2), and keeping all their other parameters, we get a much more reasonable number,  $\lambda_p = 1.61$ , not far from the value of 1.51 obtained in [16]. However, the SF model adopted in [17] cannot be considered as proven. It is based on the disputable assumption that the upturn of the specific heat quotient at low temperature and high magnetic field is due to the paramagnon contribution to specific heat, but there many other explanations of this effect. 25 K seems to be unrealistically soft. Also, low  $T_c$  and high residual resistance cast doubt on the sample quality in this study.

Here we adopt a different approach: we adopt the calculated values  $\lambda_p = 1.5$  and  $\omega_p = 131$  K, in the harmonic approximation, and total mass renormalization  $1 + \lambda_p + \lambda_s = 2.85$ , so that  $\lambda_s = 0.35$ . The results of the numerical solution of the Eliashberg equations with the  $\alpha^2 F(\omega)$  function calculated by Ignatov *et al* [16] and  $\mu^* = 0.12$  are shown in figure 2, together with the curve calculated from equation (7). In this way, we find  $\omega_s \sim 50$  K, which, we believe, is a more realistic number than 25 K. The corresponding total isotope effect coefficient is 0.75.

This may sound in agreement with the recent experiment by Klimczuk and Cava [18], who have measured the isotope effect to be 0.54 for carbon only. If the total isotope effect is 0.75, this suggests a seemingly reasonable Ni isotope effect of 0.21, suggesting that Ni phonons couple with the electrons twice weaker than C ones. Unfortunately, the first-principles calculations suggest that the Ni modes couple with electrons at least an order of magnitude more strongly than the C modes (there is hardly any C character present at the Fermi level). In the moment, the only way to reconcile this with the measurements of [18] is to assume that the observed isotope effect is a result not of the frequency shift of the C modes, but of some subtle changes in the crystal structure induced by the isotope substitution. Such a possibility is suggested by an



**Figure 2.**  $T_c$  for the electron–phonon spectral function calculated in [16] for MgCNi<sub>3</sub> (inset).

earlier study [19], where it was found that (i)  $T_c$  depends on the lattice parameter at a rate of  $\approx 310$  K  $\text{\AA}^{-1}$ , which translates an error of  $\pm 0.0015$   $\text{\AA}$  in the lattice parameter [18] into an error of  $\pm 0.46$  K in  $T_c$ , larger than the isotope shift of 0.3 K, and (ii) that two samples with the same lattice parameter and the same neutron-measured C content have  $T_c$  differing by 0.71 K. A possible explanation is that, given the proximity of MgCNi<sub>3</sub> to a ferromagnetic instability, crystallographic defects may induce local magnetic moments which, in turn, work as pair breakers. The concentration of such defects, even for the same net C content, may depend on the sample preparation and, possibly, on isotope substitution.

Therefore further studies of the isotope effect both on C and on Ni are necessary, in particular combined with accurate measurements of the isotope shift of the phonon modes.

## Acknowledgments

We are grateful to S Y Savrasov for useful discussions and for providing the results of calculations of the electron–phonon spectral function in MgCNi<sub>3</sub>. We acknowledge support from the NWO-RFBR grant 047.016.005 and from the NSF DMR grants 0342290 and 023188.

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