Physica C 515 (2015) 41–48

Contents lists available at ScienceDirect

Physica C

journal homepage: www.elsevier.com/locate/physc

Discrepancy between theory and measurement of superconducting vanadium

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ARTICLE INFO

Article history:
Received 17 December 2014
Received in revised form 26 March 2015
Accepted 23 May 2015
Available online 28 May 2015

Keywords:
Vanadium
Phonons
Electron pairing
Coulomb pseudopotential
Superconductivity prediction

ABSTRACT

We have extracted consistent phonon dispersion information out of rather inconsistent vanadium X-ray scattering data from synchrotron and vacuum tube sources. With this and a new theoretical approach we have made firm predictions for the tunnelling conductance of superconducting vanadium; it is in unusually poor agreement with experimentally measured values. We argue that the problem lies in the experimental measurement rather than the theory. The preparation of a suitable high quality tunnel barrier on vanadium represents an outstanding challenge.

1. Introduction

Some time ago we identified a fundamental conceptual difficulty in the Bardeen–Cooper–Schrieffer (BCS) theory of superconductivity [1,2]. Independently, in a thorough review of the theory, Hirsch concluded that it "is fundamentally flawed" and "may be destined to be overhauled just as other established scientific theories of the past have been overhauled" [3]. Later we explained the conceptual difficulty in BCS with a more concise argument and proposed a new scheme for pairing electrons to circumvent it [4,5].

Very recently we introduced a new theoretical procedure to determine the Coulomb pseudopotential, μ^*, in the Eliashberg–Nambu equations [6]. With these advances we made firm first principles predictions of tunnelling conductance and the zero temperature superconductive energy gap edge, Δ_0, for niobium, lead, tantalum and aluminium with high precision that agreed well with experiment [6]. In addition we made first principles predictions for tungsten, iridium and molybdenum for which experimental verification is still outstanding [6].

Having experienced success with niobium and tantalum we now turn our attention to the other Group V metal, vanadium. It offers a realistic further opportunity to test the new theoretical approach in a good superconductor with $T_c = 5.38$ K, the third highest among all stable metallic elements, T_c being the transition temperature. Vanadium phonon dispersion curves are not available from neutron scattering but data from weak (X-ray tube) and bright (synchrotron) X-ray sources are accessed and discrepancies between the two cases reconciled. We make firm predictions for superconducting vanadium tunnelling conductance that disagrees significantly with the best experimental data. We suggest an explanation and potential resolution of the discrepancy.

Our article is arranged as follows: In Section 2 we present an outline of the theoretical approach based on the new electron pairing scheme and the method of determination of μ^*. In Section 3 we study vanadium phonon data from bright X-ray scattering. In Section 4 we calibrate the electron–phonon interaction in vanadium from its normal state temperature-dependent electrical resistivity data. In Section 5 we harness these developments to predict the gap edge, Δ_0, and frequency-dependent tunnelling conductivity. The outcome brings into question the result of the best experimental measurement. In Section 6 we continue our questioning with data from weak X-ray scattering. In Section 7 we substantiate the current vanadium prediction with further detail on our earlier prediction for tantalum. Discussions and conclusions are presented in Sections 8 and 9.

2. Theoretical approach

We explain the new theoretical approach in some detail for the convenience of the reader. It is designed to overcome: (1) conceptual and numerical difficulties of the BCS theory and (2) uncertainty associated with μ^*. It is justified by its highly accurate first principles calculations for superconducting niobium, lead,

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http://dx.doi.org/10.1016/j.physc.2015.05.007
0921-4534/

tantalum and aluminium. Therefore it is expected to make accurate first principles predictions for vanadium as well.

We start with the original BCS pairing scheme. In Fig. 1 we show schematically a spherical Fermi sea and a pair of electrons on its surface initially with momenta $\mathbf{k}$ and $-\mathbf{k}$. We use the grey wedges to demonstrate the range of normal electron–phonon scattering (*N*-process, shown as the solid curved arrow) over the surface. For Debye phonons the angle of the wedges, against their symmetric axes, is 78.1°, 60.0°, 51.8°, . . .with valency 1, 2, 3, . . .[7]. The end states of the *N*-process also lie on the Fermi surface [7] and are shown in Fig. 1 with momenta $\mathbf{k}'$ and $-\mathbf{k}'$.

For definiteness we consider phonons in the first Brillouin zone but place electrons in periodic zones. In Fig. 1 we use a partial circle to represent a replica of the Fermi surface in one of the neighbouring electron zones. A state on this replicated Fermi surface, for example $-\mathbf{k}'+\mathbf{G}$, is accessible via the normal *N*-process, if it is not too far away from the initial state, $\mathbf{k}$, where $\mathbf{G}$ is a crystal momentum vector. Since $-\mathbf{k}'+\mathbf{G}$ is just a replica of $-\mathbf{k}'$, we have actually arrived at $-\mathbf{k}'$ again via an alternative passage known as umklapp scattering (*U*-process) shown by the dashed curved arrow in Fig. 1.

Now we have a dilemma. Let $h(\mathbf{k}')$ and $h(-\mathbf{k}')$ be pair occupation probability at $\mathbf{k}'$ and $-\mathbf{k}'$ respectively. On the one hand symmetry of the BCS pairing scheme dictates that $h(\mathbf{k}')$ and $h(-\mathbf{k}')$ must be equal. On the other hand $h(\mathbf{k}')$ and $h(-\mathbf{k}')$ can each arise from the *N* and *U*-processes, respectively, so that they need not and in general will not be equal. Which scenario should we follow? That is the dilemma [1].

This dilemma has an alternative manifestation. In BCS theory in its original form a trial electron wavefunction (ground state) has to be formulated in order to reveal the superconductive energy gap by variation. When an end electron state, say $-\mathbf{k}'$ in Fig. 1, is accessed from the initial state $\mathbf{k}$ via umklapp scattering (dashed curved arrow), and from $-\mathbf{k}$ via normal scattering (motion symmetric to the solid curved arrow), the exclusion principle can be violated. Consequently we will not be able to normalise the wave function, see [5] for details.

The BCS pairing scheme has a further difficulty: it leads to inconsistent first principles calculations in the normal and superconducting states. Examples in the literature are numerous with a clear pattern. In a BCS superconductor the strength of the pairing interaction is measured by the electron–phonon spectral density, $\alpha^2F(\nu)$, which can be evaluated with the atomic pseudopotential, $V(r)$, and phonon knowledge, see [8] for details. In the literature whenever $\alpha^2F(\nu)$ has been found to be reasonable, the normal state electrical resistivity, $\rho(T)$, is always too low [9,10]. Conversely but equivalently, whenever $\rho(T)$ has been found to be reasonable, $\alpha^2F(\nu)$ is too high [12,13,11]. To our knowledge there have been no exceptions.

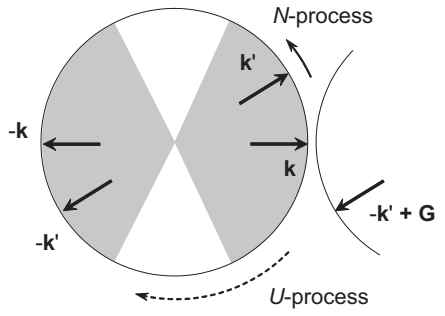

Fig. 1. Schematic of a spherical Fermi surface and a pair of electrons with initial momenta $\mathbf{k}$ and $-\mathbf{k}$. The end states within the grey wedges, with momenta $\mathbf{k}'$ and $-\mathbf{k}'$, are accessible via normal scattering. The *N*-process can drive an electron from $\mathbf{k}$ to $-\mathbf{k}'+\mathbf{G}$ in the neighbouring Brillouin zone. Therefore $-\mathbf{k}'=(-\mathbf{k}'+\mathbf{G})-\mathbf{G}$ is the end state of both normal and umklapp scattering.

The above inconsistency is also evident in [14] where Savrasov and Savrasov calculated both $\rho(T)$ and $\alpha^2F(\nu)$ from first principles for metals including aluminium, lead, vanadium, niobium and tantalum. In general, calculated $\rho(T)$ is weaker than experimental values, significantly in the case of lead. In contrast calculated $\alpha^2F(\nu)$ is always too strong, by a factor 2 or 3 times in places, compared with experimental values, including in the case of lead.

To tackle the two problems in one measure, we proposed the new pairing scheme [4,5]. We disallow superconductive pairing interaction when normal and umklapp scattering coexist (umklapp cancellation). Superconductivity then arises solely from residual umklapp electron–phonon scattering, that is when scattered electrons land on the circumference lying between the two grey wedges in Fig. 1. This not only circumvents the umklapp dilemma but also curtails excessive phonon contributions in the superconducting state. We scrutinised the idea quantitatively. We extracted via inversion nearly identical $V(r)$ from the normal state resistivity and superconducting state tunnelling data when the new pairing scheme is in place. Sample metals include niobium, lead, tantalum and aluminium [4,5].

Very recently we went a step further: we no longer rely on the tunnelling data as a reference. In addition we also follow a path to eliminate the arbitrariness in having an adjustable μ^* [6]. We aim to predict the zero temperature gap edge, Δ_0, that has not been measured in most metals. We start with $V(r)$ extracted from the resistivity data. We calculate $\alpha^2F(\nu)$ from first principles with our pairing scheme in place. We assume a reasonable Δ_0 at $T=0$ and solve the Eliashberg–Nambu equations, with tentative values of μ^* until the equations yield the assumed Δ_0, that in turn leads to a value of T_c. We adjust the Δ_0 assumption until T_c meets its experimental value, with consequent firm predictions for μ^* and Δ_0. These are highly accurate when compared with measured values in niobium, lead, tantalum and aluminium. We also made predictions for tungsten, iridium and molybdenum ready for experimental verification [6].

3. Phonons from bright X-rays

The study of phonons in vanadium has an unusually long history. To our knowledge the first inelastic neutron scattering measurement was published in 1955 by Brockhouse [15] followed by numerous other authors, see [16] and the references therein. The metal is an incoherent scatterer so that, apart from a general distribution of phonon states, it is difficult to extract more specific information about phonon dispersion from the neutron scattering data. However, in a groundbreaking study in 1970, Colella and Batterman [17] determined phonon dispersion in major symmetric directions in vanadium by means of thermal diffuse X-ray scattering, see [18,19] for further references. With the advent of bright X-rays from synchrotron radiation facilities, vanadium phonons are now measured with renewed vigour at both ambient and high pressures [20,21].

Data from X-ray scattering serve as sample points that can be utilised in fitting the data to the (Born-von Karman) theory of lattice vibrations. The fit must be of high accuracy if it is to achieve reliable first principles evaluation of normal state resistivity and superconducting tunnelling conductivity. Bosak et al. interpolated their data in the [0, 0, ζ], [ζ, ζ, 0], and [ζ, ζ, ζ] directions graphically as a guide to the eye but without actually performing numerical analysis [21]. We numerically fit their data along the same directions. For this we employ a central force model with 40 adjustable parameters for 20 neighbouring atomic shells, see [8] for details.