Evidence of nonphononic superconductivity in Nb_3Ge

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We present the results of a quantitative test to separate phononic from nonphononic contributions to the superconductivity in $A15$ Nb_3Ge. This test is based on analysis of heat capacity and tunneling $\alpha^2F(\omega)$ data and neutron-scattering data. We obtained evidence for a substantial contribution of a nonphononic mechanism to the superconducting state in Nb_3Ge. In contrast, our results suggest the superconducting state in Pb and V_3Si is due to phonons.

INTRODUCTION

For many years there has been considerable theoretical work done on the possibility of nonphononic mechanisms that could give rise to superconductivity.[1-7] This interest has greatly intensified with the discovery of the new class of high-T_c superconductors.[8] However, there has been no direct *experimental* evidence for the existence of a nonphononic mechanism that gives rise to superconductivity. In part, the problem is that even if there were a nonphononic mechanism present in a superconductor, how would that be experimentally verified? Note that a small (or even zero) value for the isotope effect need not imply nonphonon superconductivity.[9] A concept of coexistence along with a method for separation of phonon and nonphonon mechanisms was proposed recently by one of us.[10] In this paper we describe the analysis of several systems (Pb, V_3Si, and Nb_3Ge). Our main result is to give evidence that Nb_3Ge is a nonphonon superconductor. We think this is a first experimental observation of nonphononic superconductivity.

THEORY

The method requires measuring tunneling $\alpha^2F(\omega)$, heat capacity, and neutron scattering on the same material. The basic idea was that from the tunneling $\alpha^2F(\omega)$ data the electronic component of the heat capacity can be calculated (see Ref. 10):

$$C_e(T)=\gamma(T)T,\quad \frac{\gamma(T)}{\gamma(0)}=1+\rho\left[\frac{\kappa(T)}{\kappa(0)}-1\right], \qquad (1)$$

where $\gamma(0)=m^*(0)p_F/3$; $m^*(0)$ is the renormalized value of the effective mass given by $m^*(0)=m^b(1+\lambda)$ where m^b is the band value of the electron mass. $\rho=\lambda/(1+\lambda)$ and

$$\lambda=2\int d\omega\,\alpha^2F(\omega)\omega^{-1},$$

$$\kappa(T)=2\int d\omega\,\alpha^2F(\omega)\omega^{-1}Z(T/\omega)$$

[note $\kappa(0)=\lambda$], where $Z(x)$ is a universal function given in Refs. 10 and 11 (see Fig. 1). One can see from Eq. (1) that the electron-phonon interaction and the effect of thermal phonons leads to a deviation of the electronic heat capacity from a linear law.

Another quantity affected by the electron-phonon interaction (EPI) is the effective mass which becomes temperature dependent.[11-13] This can be detected by cyclotron-resonance measurements. The dependence is described by the expression:

$$\frac{m^*(T)}{m^*(0)}=1+\rho\left[\frac{\phi(T)}{\phi(0)}-1\right],$$

$$\phi(T)=2\int\frac{d\omega}{\omega}\alpha^2F(\omega)g(T/\omega),$$

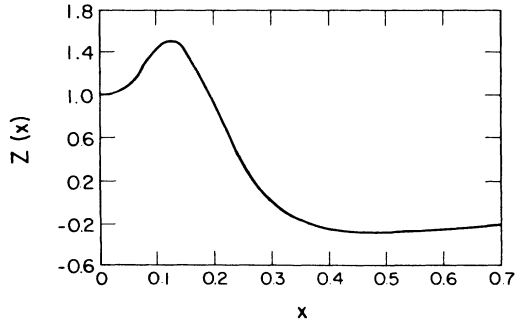

FIG. 1. The universal function $Z(x)$ used in calculating the electronic heat capacity from tunneling $\alpha^2F(\omega)$. In our case $x=T/\omega$. Note $Z(x)$ has positive and negative values.

where $g(x)$ is a universal function given in Ref. 12. Depending on the experimental situation the analysis of $m^*(T)$ can be used (as in the case for lead—see below) to determine phononic versus nonphononic contributions.

The Eliashberg equations, which generate the electron-phonon spectral function $\alpha^2F(\omega)$ through an inversion procedure,[14] assume only phonon mechanisms are contributing to the superconducting state. If there are nonphononic contributions as well (we consider the case that the nonphonon modes are located outside the region corresponding to phonon energies) the resulting $\alpha^2F(\omega)$ would be distorted. This is because while the nonphononic interaction would affect the gap function the inversion program would be trying to solve the equations using only phonon contributions. The phonon peak positions would be correct but their amplitudes and shapes would not. Thus when the electronic heat capacity is calculated [with the use of Eq. (1)], this distortion would introduce an error which could be either positive or negative [because $Z(x)$ has both positive and negative values]. Note, if the nonphonon modes are located in the frequency region within the tunneling range they can be seen directly. In this case, separation can be based just on the comparative analysis of the neutron and tunneling data.

The electronic heat capacity can also be determined by first measuring the total heat capacity then subtracting off the lattice contribution.[15–17] The lattice contribution can be calculated (Refs. 15–17) from the phonon spectrum $F(\omega)$, measureed by neutron scattering:

$$C_{\rm ph}(T)=3R\int\frac{(\omega/T)^2e^{\omega/T}}{(e^{\omega/T}-1)^2}F(\omega)d\omega\,.$$

Hence the electron heat capacity and its deviation from a linear law can be determined with the use of two independent methods [calculation from tunneling $\alpha^2F(\omega)$, and the experimental measurement]. In the absence of a nonphononic mechanism we should obtain the same result. A similar conclusion can be drawn from the analysis of the effective-mass temperature dependence (using cyclotron-resonance data). A noticeable discrepancy is a manifestation of a nonphonon contribution.[10]

Note that the nonphononic interaction (NPI) also contributes to $C_e(T)$. However, this contribution is small if $T\ll\Delta\epsilon_e$ [$\gamma'_{\rm NPI}\sim(T/\Delta\epsilon_e)^2$; $\Delta\epsilon_e$ is the characteristic energy of the virtual electron transitions; note that $\Delta\epsilon_e\gg\omega_D$]. One should distinguish the contributions of NPI to $C_e(T)$ and to Cooper pairing. The second can be very noticeable. The situation is analogous to the effect of EPI: In the region $T\to 0$ the effect of EPI on $C_e(T)$ is small[18] [$\sim(T^2/\Omega_D^2)\ln(\Omega_D)/T$]; however, EPI plays a key role in the pairing. Virtual transitions in the phonon subsystem providing the pairing and the contribution of EPI to the thermodynamic properties are described by different regularities. An analogous situation appears for NPI, and we would like to emphasize that NPI, connected with interaction of different electron groups, makes a much more noticeable contribution to the pairing than it does to $C_e(T)$.

Thus any nonphononic contribution should result in a discrepancy between the calculated and experimental $C_e(T)$. If this discrepancy is greater than the experimental uncertainty of the measurements, it means that the material is exhibiting nonphononic superconductivity.

The proposed method intended for determination of the contribution of NPI is based on the substantial progress in tunneling spectroscopy. Use of artificial barriers and the development of proximity electron tunneling spectroscopy allow the determination of the function $\alpha^2F(\omega)$ for complicated materials.

There are complications that arise. Ideally the three measurements should be done on the same sample (to make sure that any discrepancy is not due merely to sample differences), but this would be very difficult. Tunneling $\alpha^2F(\omega)$ measurements require thin-film superconductors, while neuron scattering requires bulk samples (heat capacity can be done on either). Even if it all could be done on the same sample, tunneling measures only the very surface of the material, whereas both heat capacity and neutrons scattering are bulk measurements. Furthermore, in the case of compounds, neutron scattering does not produce directly the phonon density of states $F(\omega)$ (which is what is required for the lattice contribution) but some related function $G(\omega)$. The difference between them can be estimated (see, for example, Ref. 19), and this should be taken into account. As a result of these complications, a substantial discrepancy (exceeding experimental error) must be seen to claim evidence for nonphononic superconductivity. In addition to Nb_3Ge, we studied the superconductors Pb and V_3Si. In both of these latter cases the deviation was small (see below). This can be considered as an additional verification of the method.

Pb AND V_3Si

Let us first describe our results for Pb and V_3Si. Analysis based on the methods described above indicate that superconductivity for both materials is caused by the phonon mechanism (although V_3Si might have a small nonphononic contribution).

For Pb we used the calculation of the temperature dependence of effective mass,[11] which gives excellent agreement with experimental data from cyclotron-resonance measurements[20] as can be seen in Fig. 8 of Ref. 11. This provides strong evidence that the superconductivity in Pb is due to the conventional phonon mechanism.

We also analyzed data for lead to determine the electronic heat capacity, where we used the tunneling $\alpha^2F(\omega)$ obtained by McMillan and Rowell,[14] the neutron-scattering data from Stedman, Almqvist, and Nilsson,[21] and the heat-capacity data from Meads, Forsythe, and Giaugue.[22] Note that the use of cyclotron-resonance data for Pb is more effective than heat-capacity data. This is because the heat capacity is dominated by the lattice contribution even at relatively low temperatures (lead has a Debye temperature of about 100 K). Thus calculating the electronic heat capacity requires subtracting two large numbers resulting in a very small one. This gives an uncertainty that is greater than the number itself. The results of this analysis for lead are given in Table I.

While not relevant to the question of nonphononic superconductivity, there is good agreement (within 10%) between the measured total heat capacity and the sum of the electronic and the lattice heat capacity. This is an impor-

TABLE I. Experimental and calculated heat-capacity values for lead. The heat-capacity values are all in mJ/mol K. Note the last column is C_e+C_p to compare with C_{total}.

T (K)	C_{total}	C_p [from $F(\omega)$]	C_e [from $a^2F(\omega)$]	C_e+C_p
15	7233	7651	30	7681
20	11018	11767	29	11796
25	14065	15075	29	15104
30	16505	17582	32	17614

tant demonstration of the consistency betweeen the heat-capacity and neutron-scattering measurements.

Consider now V_3Si. This material can be analyzed with the same method using heat capacity as was used for Nb_3Ge (see below). V_3Si is also an $A15$ compound with a lower T_c (17 vs 23 K) but with a substantially higher density of states. Thus V_3Si seems less likely to have a nonphononic contribution to the superconductivity. In addition, V_3Si is an equilibrium compound, thus sample differences are less likely to be critical. The heat-capacity data ($T_c=16.8$–17.3 K) is from Viswanathan and Caton,[23] the neutron-scattering data ($T_c=16.7$ K) is from Schweiss *et al.*,[24] and the tunneling $a^2F(\omega)$ data ($T_c=15.4$ K) is our own.[25] Table II gives the relative values for C_e at 30 and 25 K as calculated from tunneling $a^2F(\omega)$ and determined using heat-capacity and neutron-scattering measurements for V_3Si.

For V_3Si there is some discrepancy between the calculated and experimental electronic heat capacities, but it potentially can be explained by experimental error (roughly 20%—this will be discussed more fully in the Nb_3Ge section). It is important to note that we focused on the temperature dependence of the heat capacity, in particular the ratio $C_e(30\text{ K})/C_e(25\text{ K})$. This allows us to exclude the unknown $\gamma(0)$ factor The choice of temperature is dictated by the need to be above T_c (we are looking at the normal-state heat capacity) and the availability of heat-capacity data.

NONPHONON CONTRIBUTION TO SUPERCONDUCTIVITY IN Nb_3Ge

The choice of Nb_3Ge was based on several factors. Until recently, Nb_3Ge had the highest transition temperature known (a record it held for 13 years). Klein *et al.*[26] made band-structure calculations on many of the $A15$ compounds and in all cases but Nb_3Ge found their calculations consistent with the observed transition temperatures. Nb_3Ge was anomalous in having a high T_c but a low value (relative to other high-T_c $A15$ compounds[27]) for $N(0)$, the density of states at the Fermi level. Band structure makes the "demon" mechanism favorable.[2,6,26] Of course the high T_c of Nb_3Ge can be explained by other reasons such as mode softening,[28,29] but the above arguments make Nb_3Ge a good candidate to test for nonphononic superconductivity.

Tunneling $a^2F(\omega)$ and heat-capacity data were available for the same sample[29] (which had a T_c of 20.3 K). Neutron-scattering experiments were done on Nb_3Ge with a T_c of 20 K by Muller *et al.*[19] We believe this was as close to doing the test on one sample as was experimentally possible for a compound at present. The error between $F(\omega)$ and $G(\omega)$ (which arises in a compound due to the different ratios of nuclear cross section to mass for the component elements) for Nb_3Ge from neutron scattering was estimated by Muller *et al.*[19] to be 10%. They also calculated the lattice contribution to the heat capacity which agreed with our results.

Table III gives the relative values for C_e at 30 and 25 K as calculated from tunneling $a^2F(\omega)$ and determined using heat-capacity and neutron-scattering measurements for Nb_3Ge.

The sources of error include uncertainties in the original experimental data which in all three measurements was about 10%. This could account for roughly a 20% uncertainty in the comparison of the electronic heat capacities. The use of different samples may introduce a somewhat greater uncertainty but it is difficult to quantify. In the case of V_3Si the discrepancy is potentially explainable from experimental error (although a nonphononic contribution is not ruled out), but for Nb_3Ge the difference is beyond reasonable experimental error. While this method does not specify what mechanism may be at work (i.e., virtual transitions in the presence of overlapping bonds,[2] "demons,"[2,6] etc.), it is suggestive that there is a substantial nonphononic contribution to the superconductivity in Nb_3Ge.

CONCLUSIONS

In this paper we carry out analysis to obtain experimental evidence for a nonphononic mechanism. Our approach is based on the method proposed in Ref. 10. The approach can be used for different materials. As the experimental data becomes available it would be interesting to apply this analysis to look for the possible contribution of high-energy modes to the superconductivity of the oxide superconductors.

The main results of this paper can be summarized as follows.

(1) The method of separation of phonon and nonphonon contributions is described. The method is based on the analysis of tunneling, heat-capacity, and neutron-scat-

TABLE II. Relative values of the electronic heat capacity between 25 and 30 K for V_3Si.

Compound	Calculated $C_e(30\text{ K})/C_e(25\text{ K})$	Experimental $C_e(30\text{ K})/C_e(25\text{ K})$	Percent difference
V_3Si	1.19	1.40	18%

TABLE III. Relative values of the electronic heat capacity between 25 and 30 K for Nb_3Ge.

Compound	Calculated $C_e(30\ K)/C_e(25\ K)$	Experimental $C_e(30\ K)/C_e(25\ K)$	Percent difference
Nb_3Ge	1.07	1.63	52%

tering data. We think that the experimental data used in our analysis are reliable enough to draw our conclusions. A nonphonon mechanism is manifested as a difference of the dependence $C_e(T)$ [and $m^*(T)$] obtained by two independent methods.

(2) The analysis of Pb and V_3Si, which are known to be superconductors with phonon mechanisms, indeed show only small differences. This is evidence that their superconducting state is due to the electron-phonon interaction. This analysis is an additional justification of the validity of the method.

(3) The results of the analysis suggest that there is a substantial nonphononic contribution to the superconductivity in Nb_3Ge. We think that this is the first experimental observation of a nonphonon contribution to superconductivity.

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