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## ABSTRACT

Far infrared techniques in the range  $10$  to  $200\text{ cm}^{-1}$  ( $1$  to  $25\text{ meV}$ ) will be used to examine the high temperature superconductors  $\text{V}_3\text{Si}$ ,  $\text{Nb}_3\text{Ge}$ , and  $\text{Nb}$ , and the high-temperature granular superconductor  $\text{NbN}$ . Fourier and laser spectrometers and the new technique of laser thermal spectroscopy will yield information about the electron-phonon spectral function, the temperature dependence of superconducting properties, and other fundamental aspects of high temperature homogeneous and inhomogeneous superconductors. A detailed theoretical analysis will complement the experimental work. The information gained may help in the basic understanding of high temperature superconductivity and in the development of improved superconducting materials for applications.

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## INTRODUCTION

High temperature superconductors have gap energies which lie well within the far infrared range 10 to 200  $\text{cm}^{-1}$ , and spectroscopy in this region is an effective tool for probing these materials. Since the high temperature materials, especially the A-15 family, are not yet fully understood and offer important technical potential their study in the far infrared is well worthwhile. Although far infrared methods were used early in the investigation of superconductivity<sup>1</sup> recent advances in instrumentation--notably Fourier transform spectroscopy<sup>2</sup> and the advent of the far infrared laser<sup>3</sup>--have vastly increased the scope of possible experiments.

Far infrared methods can also contribute to another current area of superconductor research, that of inhomogenous or granular systems.<sup>4</sup> Some of these systems include high-temperature superconductors such as  $\text{V}_3\text{Si}$  or  $\text{NbN}$ . The granular systems are of major fundamental importance because of the many unanswered questions about grain-to-grain coupling and the possibilities of one- and two-dimensional behavior. There are also strong device possibilities on two fronts. First, the extra degree of freedom involved in mixed systems like a superconductor/insulator combination encourages new kinds of material tailoring as has been discussed by Tsuei.<sup>5</sup> Second, any system which may in some respect contain a large number of coupled Josephson oscillators has most intriguing possibilities for microwave/millimeter wave devices. The presence of Josephson coupling may also produce far infrared phenomena. Virtually no far infrared work has been done in high temperature granular systems.

This proposal reviews a year's activity under Department of Energy auspices in the far infrared study of the high temperature superconductors  $V_3Si$ ,  $Nb_3Ge$ ,  $Nb$ , and granular  $NbN$ . Following the progress report a proposal for a second (renewal) year will be presented.

#### PROGRESS REPORT

Activities in the contract year now ending include: the first laser thermal spectroscopy measurements in  $V_3Si$ ,<sup>6</sup> establishing the validity of this new method and giving additional information about this important A-15 compound; the initiation of detailed theoretical analyses of our data to give more reliable values of the electron-phonon spectral function  $\alpha^2F(\omega)$  and to confirm the validity of our experimental methods; the first far infrared transmission measurements in  $Nb_3Ge$ ; the launching of an effort in high temperature granular materials with the first far infrared measurements in granular  $NbN$ ; and the improvement of our far infrared instrumentation to give better data.

##### 1. Laser thermal spectroscopy in $V_3Si$

In this method, the sample is irradiated with one of the fixed frequencies available from our optically pumped far infrared laser while the temperature is swept through  $T_c$ . Thus the high laser power can be used to give an excellent signal-to-noise ratio while the temperature variation of the gap provides a form of continuous tunability. We have successfully analyzed two thin film samples of  $V_3Si$  in this way. The laser frequencies were set within the critical regimes  $\hbar\omega \ll 2\Delta$ ,  $\hbar\omega \approx 2\Delta$ , and  $\hbar\omega \gg 2\Delta$  while the temperature was swept from 5 to 20 K. The onset and disappearance of superconducting behavior could be clearly and

beautifully seen in these runs with excellent signal-to-noise values.

We have analyzed the data with the BCS theory in the dirty limit and find that although a main peak at the correct gap energy can be so explained, there remain several anomalous features. The observed temperature dependence of the gap is not BCS-like, and structure other than the main peak is observed. These anomalies may be connected with the fact that, as has been shown earlier,<sup>7</sup> these samples are not truly in the extreme dirty limit and finite scattering time effects are significant. The anomalous features also suggest the presence of a second gap and possibly some electron-phonon behavior. These results and other data in NbN (to be described later) show that laser thermal spectroscopy is a useful tool.

## 2. Theoretical analysis of $\alpha_{tr}^2 F(\omega)$ in $V_3Si$

We previously published a detailed analysis of normal state far infrared transmission in  $V_3Si$ <sup>8</sup> which, using Allen's formulation for Holstein processes,<sup>9</sup> yielded the transport electron-phonon spectral function  $\alpha_{tr}^2 F(\omega)$ . Relative to the phonon function  $F(\omega)$  from neutron-scattering data our derived  $\alpha_{tr}^2 F(\omega)$  showed a general shift to lower energies and the emergence of an additional low energy peak at 6 mV. These low energy enhancements appeared to be critical in the superconducting behavior of  $V_3Si$ , but it would be very desirable to confirm them by other evidence.

We had earlier published superconducting and normal absorption data for good quality bulk  $V_3Si$ .<sup>10</sup> These results showed significant structure which is also apparently related to the electron-phonon function. These

data were then only sketchily analyzed, but in the past year we have started to make a detailed fit to them. We use Allen's simple theory<sup>9</sup> which is not wholly correct in the superconducting strong coupling limit but which has nevertheless worked well in explaining far infrared results in lead, a strong-coupling material. The analysis is not complete but to date it confirms the shift to lower energies, although the role of the 6 mV peak is unclear.

This theoretical effort can be carried out because we have acquired a theoretical post-doctoral research associate, G. De. Although she has been able to provide only a part-time effort so far, she gives us an important analytical capability.

### 3. Far infrared transmission in Nb<sub>3</sub>Ge

We have used the far infrared laser to measure the superconducting to normal transmission ratio  $T_s/T_n$  for one film of Nb<sub>3</sub>Ge with frequencies between 11.2 and 104 cm<sup>-1</sup>. The results seem to exhibit smaller structure than BCS theory predicts, but the data have not yet been extensively analyzed.

### 4. Far infrared laser thermal spectroscopy in granular NbN

NbN was chosen for an initial examination because of its high  $T_c$  ( $\approx$  15.5 K) and because an excellent suite of samples was available from D. Gubser and S. Wolf of the Naval Research Laboratory. The samples are made with a variety of grain sizes and separations so that the inter-grain coupling varies.

An important feature of granular NbN is the existence of several characteristic temperatures. In recent DC measurements Gubser et al.<sup>11</sup> have observed structure at temperatures denoted as  $T_{cg}$ , identified as the superconducting transition temperature for individual grains;  $T_{cj}$ , identified as the temperature of the two-dimensional phase ordering transition; and  $T^*$ , where a sharp increase in the critical current is observed.

In our search for these critical temperatures we examined one sample of NbN, with a surface resistance of 6000 ohm/square, with laser thermal spectroscopy. Transmission data were taken between 11.2 and  $10^4$   $\text{cm}^{-1}$  as the temperature was swept from 5 to 20 K. Parallel data were taken with our Fourier transform system. The Fourier results confirmed the laser data, although the signal-to-noise was much inferior.

The initial analysis of the data is very encouraging. The presence of the superconducting transition for the individual gaps is definitely seen with more clarity than in the DC data and this alone is a worthwhile result. In addition a second well-defined peak occurs at a lower temperature  $\approx T_{cj}$ . Our data may not go to a low enough temperature to include  $T^*$ , but a third feature is observed which has no parallel in the DC results.

##### 5. Instrumentation improvements

Both the Fourier and the laser systems have received attention in the past year which should lead to improved signal-to-noise ratios in our experiments. The Fourier optics have been redesigned to allow

substantially greater throughput for transmission measurements, and we have ordered a cooled detector. The output quality for the far infrared optically pumped laser depends critically on the pumping CO<sub>2</sub> laser. The latter has been overhauled and more massive optical mounts for the grating and mirrors have been installed. As a result the power output has increased by some 20% and the output signal is noticeably more stable.

#### PROPOSAL FOR THE COMING YEAR

Most of the lines of research explored in the past year appear promising and set natural directions for future work, as described below.

1. Further far infrared measurements and analysis in V<sub>3</sub>Si, Nb, Nb<sub>3</sub>Ge, and NbN

We will continue the detailed analysis of the V<sub>3</sub>Si results where we have extensive bulk and thin film data to give a definitive  $\alpha_{tr}^2 F(\omega)$ . Unless the analysis indicates the need for more data, no further measurements will be made in V<sub>3</sub>Si.

The next priority would be Nb, because the analysis should provide a good test of our analytical methods and because of the long-standing interest in its  $\alpha^2 F(\omega)$ . We already have data on one thin film sample and will examine a second one of somewhat better quality which is on hand.

The Nb<sub>3</sub>Ge measurements are especially difficult because the samples have exceptionally low transmissions. We will attempt an analysis of the data on hand and then make a judgement as to whether further

measurements are necessary.

The NbN results to date can be considerably clarified by examining at least one more sample with different coupling behavior. We recognize that the granular materials have many complexities, some of which may not much illuminate the basic superconducting behavior. The high level of basic interest and the possible technical applications justify some effort in the next year but this effort will not be allowed to overshadow the work on the homogenous materials.

## 2. Further development of laser thermal spectroscopy

The laser thermal method worked well in  $V_3Si$  and NbN, where it proved capable of following superconducting behavior in detail. Added sensitivity could be gained by modulating the sample temperature so that one could directly measure the derivative of far infrared transmission with respect to temperature. Excellent temperature stability and control are required and appropriate equipment has been requested in this proposal. An additional factor is the need to provide a simple means to modulate the sample temperature at a frequency high enough for practical lock-in detection. We have devised a method which should work reliably with virtually no modification in the samples or in their mounting, and will implement it this year.

## 3. Continuing theoretical analysis of far infrared data

We anticipate a strong interaction between experiment and theoretical analysis in the coming year and request funds for both experimental and theoretical post-doctoral support. Because far infrared methods are not

as well established as tunneling careful theoretical analysis is needed to help confirm their validity. Also many of the necessary calculations--for instance, the optical response of a BCS superconductor for arbitrary temperature and scattering time--simply do not exist in the literature. Thus extensive theoretical activity is necessary to support the experimental effort.

For data analysis where  $\alpha^2F(\omega)$  enters, we will use the Allen formulation for at least a first look at the data. If Allen's theory appears to fail we will turn to the far infrared calculations of Swihart and co-workers.<sup>12</sup> In recent work<sup>13</sup> they have reported increasing success in detailed fits for lead as they take into account vertex corrections for the theory of Holstein processes. We have maintained contact with Professor Swihart and are assured of his continuing interest in our data for  $V_3Si$  and Nb.

We will use our measured values of  $\alpha^2F(\omega)$  to derive superconducting parameters such as the coupling constant via the McMillan<sup>14</sup> approach, thus making the connection between optical results and basic superconducting behavior. Some effort in the theory of granular materials will also be necessary to interpret the NIN results.

#### 4. Further improvements in far infrared instrumentation

Because far infrared measurements are made in an extremely difficult region of the spectrum, we consider improvements in the far infrared instrumentation an important continuing part of our activity. Next year we intend to: install a more powerful and stable power supply for the pumped laser; install the newly designed high throughput optical system in the Fourier spectrometer; and provide on-line data analysis for the Fourier spectrometer.

## 5. Possible interactions with optical research elsewhere

The research reported and proposed here appears to be the only recent work carried out near the gap energy and aimed at determining  $\alpha^2F(\omega)$ . Nevertheless, other recent optical work elsewhere may be relevant to the proposed activities. Tanner et al. have made far infrared measurements<sup>15</sup> in a low  $T_c$  granular system, Sn in a KCl matrix, with puzzling features that may also occur in our NbN data. Professor Tanner will also begin a series of far infrared Fourier measurements in Nb<sub>3</sub>Sn and will eventually provide these samples for examination by our laser. Raman scattering has been carried out in V<sub>3</sub>Si by Schickanz et al.<sup>16</sup> and by Klein and co-workers.<sup>17</sup> Both groups observed the  $E_g$  optical phonon near 300 cm<sup>-1</sup>. Recently Klein and co-workers reported phonon hardening observed by Raman scattering in proton-irradiated V<sub>3</sub>Si.<sup>18</sup> These high frequency results may eventually connect with our low frequency electron-phonon information. Klein has also reported on Raman studies in superconducting 2H NbSe<sub>2</sub>,<sup>19</sup> where charge density waves appear to play an important role. We have discussed with Professor Klein whether far infrared measurements might add to the understanding of this behavior.

## REFERENCES

1. M. Tinkham in Far Infrared Properties of Solids, S. S. Mitra and S. Nudelman, Editors (Plenum Press, New York, 1970), p. 223.
2. P. L. Richards in Spectroscopic Techniques, D. H. Martin, Editor (Wiley, New York, 1967), p. 33.
3. T. Y. Chang, IEEE Trans. Microwave Theory and Techniques MTT-22, 983 (1974); B. L. Bean and S. Perkowitz in Infrared and Millimeter Waves: Volume 2, Instrumentation, K. J. Button, Editor (Academic Press, New York, 1979), p. 273.
4. An excellent review of current activity is given in Inhomogeneous Superconductors - 1979 (AIP Conference Proceedings No. 58), D. U. Gubser, T. L. Francavilla, S. A. Wolf, and J. R. Leibowitz, Editors (American Institute of Physics, New York, 1980).
5. Ibid., p. 67.
6. G. D. Holah, D. Ogilvie, J. Reid, and S. Perkowitz in Digest of the Fourth International Conference on Infrared and Millimeter Waves, Miami, 1979, S. Perkowitz, Editor (IEEE, New York, 1979. IEEE No. 79 CH 1384-7 MTT), p. 25; S. Perkowitz, Bull. Am. Phys. Soc. 25, 333 (1980).
7. S. W. McKnight, B. L. Bean, and S. Perkowitz, Phys. Rev. B 19, 1437 (1979).
8. S. W. McKnight, S. Perkowitz, D. B. Tanner, and L. R. Testardi, Phys. Rev. B 19, 5689 (1979).
9. P. B. Allen, Phys. Rev. B 3, 305 (1971); 11, 2693 (1975).
10. M. Merlin, S. Perkowitz, and L. R. Testardi, Solid State Commun. 18, 1059 (1973).
11. See reference 4, p. 159.
12. J. C. Swihart and W. Shaw, Physica 55, 678 (1971); G. B. Arnold and J. C. Swihart, Bull. Am. Phys. Soc. 24, 505 (1979).
13. J. C. Swihart and G. B. Arnold, Bull. Am. Phys. Soc. 25, 364 (1980).
14. W. L. McMillan, Phys. Rev. 167, 331 (1968).
15. See reference 4, p. 288; G. L. Carr, J. C. Garland, and D. B. Tanner, Bull. Am. Phys. Soc. 25, 264 (1980).
16. S. Schicktanz, R. Kaiser, W. Spengler, and B. Seeber, Solid State Commun. 28, 935 (1978).

17. H. Wipf, M. V. Klein, B. S. Chandrasekhar, T. H. Geballe, and J. H. Wernick, Phys. Rev. Letters 41, 1752 (1978).
18. S. B. Dierker, R. Merlin, M. V. Klein, B. S. Chandrasekhar, and J. Blue, Bull. Am. Phys. Soc. 25, 333 (1980).
19. M. V. Klein, Bull. Am. Phys. Soc. 25, 168 (1980); R. Sooryakumar and M. V. Klein, Bull. Am. Phys. Soc. 25, 201 (1980).

## CONTRACT-SUPPORTED PUBLICATIONS AND PRESENTATIONS

1. Far Infrared Laser Thermal Spectroscopy of Superconductors, G. D. Holah, D. Ogilvie, J. Reid, and S. Perkowitz, Digest of the Fourth International Conference on Infrared and Millimeter Waves, Dec. 1979 (IEEE, New York, 1979. IEEE NO. 79 CH 1384-7 MTT), S. Perkowitz, Editor, p. 25.
2. Far Infrared Laser Thermal Spectroscopy of  $V_3Si$ , S. Perkowitz, Bull. Am. Phys. Soc. 25, 333 (1980). (Presented at the APS March meeting, New York, 1980).
3. "Far Infrared Fourier and Laser Spectroscopy," seminar presented by S. Perkowitz at Bell Telephone Laboratories, Murray Hill, NJ, June 4, 1979; and at Bell Telephone Laboratories, Holmdel, NJ, June 6, 1979.
4. "Far Infrared Spectroscopy of High Temperature Superconductors," seminar presented by S. Perkowitz at the Naval Research Laboratory, Washington, D.C., Nov. 19, 1979.

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