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Possible precursor phenomenon to superconducting transition in niobium: Anomalous behavior of shear modulus at low temperatures

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Niobium is an important superconducting element widely used in many applications. There is a long history of interest in the microscopic origins of superconducting mechanism of this material. However, the precise prediction of material specific properties of superconductors including niobium still remains one of the great challenges of modern condensed matter physics. One of the obstacles that limit us in calculating, for example, superconducting transition temperature is the lack of enough knowledge of materials in the normal state. Here the author shows experimental evidence for a precursor phenomenon to superconducting transition in niobium. The temperature variation of the tetragonal shear modulus $C'=(C_{11}-C_{12})/2$, of a single-crystal niobium in the normally conducting state under a strong magnetic field and at ambient pressure was measured by a contact-free ultrasonic method. Anomalous decrease in C', just a few degrees above the known superconducting transition temperature T_c 9.26 K, was observed and it continued to decrease down to 4.22 K, contrary to the usual tendency of the temperature variation of the elastic constants of metals, an increase with the decreasing temperature. No such anomalous decrease in elastic constants of normally conducting metallic elements at low temperatures and at ambient pressure have been observed until now. Since C' is a key factor in explaining the structural instability which is related to the strength of the electron-phonon coupling and the occurrence of high-T_c, it can be considered that the start of decrease in C' just a few degrees above the T_c, is a precursor phenomenon to superconducting transition in niobium.

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I. INTRODUCTION

Nb (niobium) has the unusually high superconducting transition temperature (9.26 K) at ambient pressure compared to all other elements in the periodic table. Nb, the crystal structure of which is bcc, is widely used in many important superconducting applications, such as making Josephson junctions in the microwave engineering and making superconducting compounds like Nb_3Sn and NbTi in the high magnetic field applications. There is a long history of interest in the microscopic origins of superconducting mechanism of this material.[1–5] In spite of the success, Eliashberg theory[6] and McMillan's formula[7] have to be considered semiphenomelogical theories. μ^* in McMillan's formula, a measure of the effective electronic repulsion, is treated as an adjustable parameter. *Ab initio* theories of superconductor, which does not contain any adjustable parameters, was recently developed,[5] but the predicted T_c and the superconducting gap of Nb differ by 10% among the three different levels of approximation. For the reasons mentioned above, further studies of this important material Nb are necessary. The purpose of this report is to demonstrate an experimental evidence of a phenomenon, a possible precursor phenomenon to superconducting transition in Nb, and to call the attention of many researchers to further studies of this important material.

II. MEASUREMENT OF ELASTIC CONSTANTS

The temperature variations of the elastic constants of Nb, were measured in the past by several researchers. But most of them did not measure the elastic constants with small enough temperature steps at low temperatures. Measurements of C' with small temperature steps were done in Refs. 8 and 9, in which no such phenomena as reported in this paper were observed. In Ref. 8, the two different techniques were used to measure C' and the two results were different, so that one cannot fully rely on the data. In Ref. 9, only the difference in C' between the normal and superconducting state of Nb was reported, so that it is not possible to tell the temperature variation of the absolute values of C'.

In this experiment, a single-crystal Nb disk (purity 99.9%, diameter 12 mm, thickness 0.512 mm, and with the surface normal [110]) was cooled from 50 down to 4.22 K in a magnetic field 0.5 T and at ambient pressure. The magnetic field was applied perpendicular to the sample surface. Since 0.5 T is very much higher than the critical field H_{c2} of Nb(0.198 T), the crystal was completely in the normally conducting state during the whole experiment.

The elastic constants were measured by resonance mode electromagnetic acoustic transducer (R-EMAT), the early and extensive works of which were done by the present author and his colleagues.[10–13] The schematic of R-EMAT used for this measurement is shown in Fig. 1. A transmitting coil (T coil, diameter 7 mm, number of turns 9.5) was placed near one surface with a gap of 0.1 mm to the sample. A similar receiving coil (R coil) was placed in a symmetrical position on the other side of the sample. ac currents in the T coil generate eddy currents near the sample surface and the mutual interaction between the eddy currents and dc magnetic field generate vibrating Lorentz force parallel to the surface and eventually shear ultrasonic waves in the sample. The R coil detects the waves through the inverse physical process. The T-coil current frequency was scanned in a 2 MHz range between 7 and 9 MHz range. During the scanning, the thickness resonance condition $kd=m\pi$ is satisfied

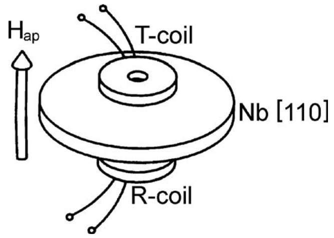

FIG. 1. Experimental setup for contact-free generation and detection of ultrasonic waves for a single crystal Nb disk in a perpendicular magnetic field (0.5 T). Since the magnetic field was much higher than the upper critical field H_{C2} of Nb(0.198 T), the crystal was completely in the normally conducting state during the whole experiment. Nb disk (purity 99.9%, diameter 12 mm, thickness 0.512 mm, and with surface normal [110]). *T* coil and *R* coil (diameter 7 mm, with 9.5 turns). Gap between each coil and the surface (0.1 mm).

for particular values of *k*, where *k* is the ultrasonic wave number, *d* is thickness, and *m* is a positive integer, thereby generating a standing wave and greatly improving the generating efficiency. This method can be applied to a superconductor in the mixed state as well as to a normally conducting metal. Detailed descriptions of the measurement method have been given for a normally conducting metal sample[10,11] and a superconducting metal sample.[12,13]

This technique is especially useful for a high precision ultrasonic measurement of a thin small sample at very low temperatures because of several unique properties of this method. This is a contact-free ultrasonic method which requires no acoustic coupling material. The acoustic properties of just only the sample can be measured because there is no coupling material. Otherwise necessary acoustic coupling material would freeze at low temperatures and it might cause undesirable effects like stress to the sample. The second advantage comes from its thickness resonance mode by which a very thin sample less than 0.5 mm thick can be measured. Another very important advantage is that it can generate and detect the three mutually orthogonally polarized ultrasonic waves simultaneously with the same setting. In the setting shown in Fig. 1 the two shear waves, polarized along [001] and $[1\bar{1}0]$ are generated by the birefringence effect of the sample anisotropy, and detected.

III. TEMPERTURE VARIATION OF ELASTIC CONSTANTS

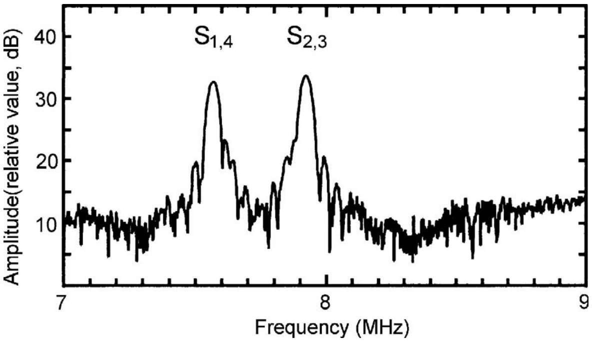

FIG. 2. Resonant peaks for contact-free ultrasonics obtained on single-crystal Nb at 4.22 K in the normally conducting state in a magnetic field 0.5 T. $S_{1,4}$ and $S_{2,3}$ are the fourth- and third-order shear resonances.

Typical data obtained are shown in Fig. 2. It was obtained at 4.22 K under applied magnetic field H_{ap} of 0.5 T. $S_{1,4}$ is the fourth-order resonance of slow shear waves and $S_{2,3}$ is the third-order resonance of fast shear waves. The resonance orders were determined by the number of resonance peaks obtained at lower frequencies. The waves corresponding to $S_{1,4}$ and $S_{2,3}$ are polarized along [001] and $[1\bar{1}0]$, respectively. These waves can be identified by their wave velocities $V=2\,fd/\mathrm{m}$, where f is the resonance frequency. The resonance frequency was determined from the average of two frequencies, one frequency corresponding to the midpoint between the two points which were lower than the resonance peak by −3 dB and one corresponding to the midpoint between the −6 dB points. The frequencies obtained at 4.22 K for $S_{1,4}$ and $S_{2,3}$ in Fig. 2 are, respectively, 7.569 and 7.924 MHz, with corresponding velocities $V_{S1}=1938$ and $V_{S2}=2705$ m/s. These velocites are nearly equal to but a little larger than the calculated velocities 1820 and 2570 m/s obtained using the known density and the single crystal elastic constants of Nb at room temperature,[14] as expected from the difference in temperature. The elastic constants C_{44} and $C'=(C_{11}-C_{12})/2$, were calculated from the relations $\rho V_{S1}^2=C_{44}$ and $\rho V_{S2}^2=(C_{11}-C_{12})/2$ using the room temperature value of mass density 8400 $\mathrm{kg/m^3}$. No correction for contraction of the sample with temperature was made since the main interest is to measure the temperature variation of C_{44} and C'. No correction for a magnetic field effect on the wave velocities was made for the same reason. Figure 3 shows C_{44} vs temperature and Fig. 4 shows C' vs temperature. In Fig. 3, C_{44} increases almost linearly with decreasing temperature with a negative slope dC/dT from 50 to 30 K,

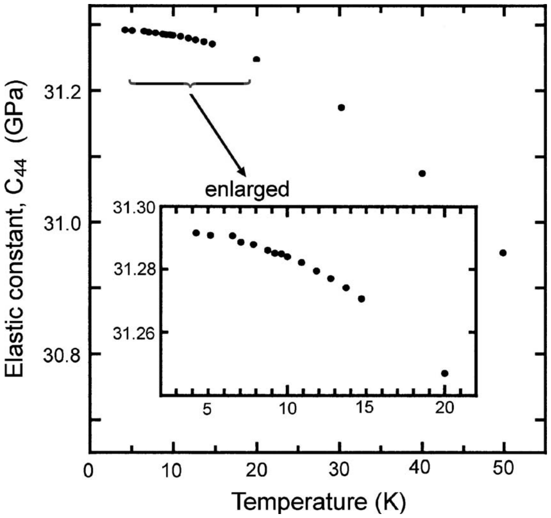

FIG. 3. Elastic constant C_{44} vs temperature measured by contact-free ultrasonics. The inset is the enlarged part between 2 and 22 K.

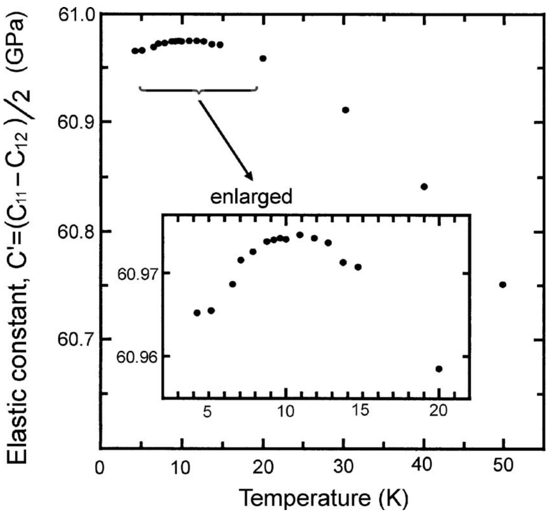

FIG. 4. Elastic constant $C'=(C_{11}-C_{12})/2$ vs temperature measured by contact-free ultrasonics. The inset is the enlarged part between 2 and 22 K.

and below 30 K the slope continuously decreases with decreasing temperature down to 4.22 K, but still keeping a negative slope. C_{44} would approach its value at 0 K with zero slope as frequently pointed out for elastic constants of normal metals. In Fig. 4, C' shows a different behavior. Between 50 and 15 K the temperature dependence of C' is similar to that of C_{44}, but just below 11 K the zero slope starts and it becomes positive, and eventually a decrease in the magnitude follows down to 4.22 K. No such anomalous decrease in elastic constants of normally conducting metallic elements at low temperatures and at ambient pressure have been observed until now.

IV. DISCUSSIONS

For the anomalous decrease of C' of the Nb crystal shown in Fig. 4, the following explanation is possible. There exists a relation between the magnitude of C' and the stability of the bcc structure, and small C' values indicate the structural instability of the transition metal bcc.[15–18] Therefore it can be considered that the beginning of decrease in C' shown in Fig. 4 signals the beginning of a lattice instability. It was shown theoretically that the strength of the electron-phonon coupling eventually leads to the lattice instability.[19] The interplay of the lattice instability and the occurrence of high-T_c have been discussed many times theoretically,[20] and experimentally[21–26] for transition metal compounds, and other compound superconductors. The above arguments about the lattice instability and high-T_c are for compound superconductors, but there is a possibility that these arguments also apply to niobium because of the same phonon-mediated superconductivity. For these reasons, it is possible to consider the anomalous decrease in C' of the niobium crystal just a few degrees above the known transition temperature is a sign of a lattice instability and an increase in the electron phonon coupling, and its becoming ready for superconducting transition as soon as the temperature drops to the transition temperature if the magnetic field strength is small enough. For some compound superconductors C' exhibits a softening at a temperature substantially higher than T_c (Ref. 27) so that it is not appropriate to call the softening a precursor phenomenon. In the case of the present experiment, it is possible to consider that the beginning of decrease in C' just a few degrees above the superconducting transition temperature is a newly discovered phenomenon, a precursor phenomenon to superconducting transition in Nb. This result appears to be important with respect to the mechanism of superconductivity of niobium and other element superconductors which have bcc structure. Detailed microscopic origin of this phenomenon found in this important material Nb needs to be investigated experimentally and theoretically.

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