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2004 J. Phys.: Condens. Matter 16 2033

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# Low-temperature specific heats of an anisotropic superconductor, $\text{Hg}_x\text{Nb}_3\text{Te}_4$

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Received 15 December 2003

Published 12 March 2004

Online at [stacks.iop.org/JPhysCM/16/2033](http://stacks.iop.org/JPhysCM/16/2033) (DOI: 10.1088/0953-8984/16/12/012)

## Abstract

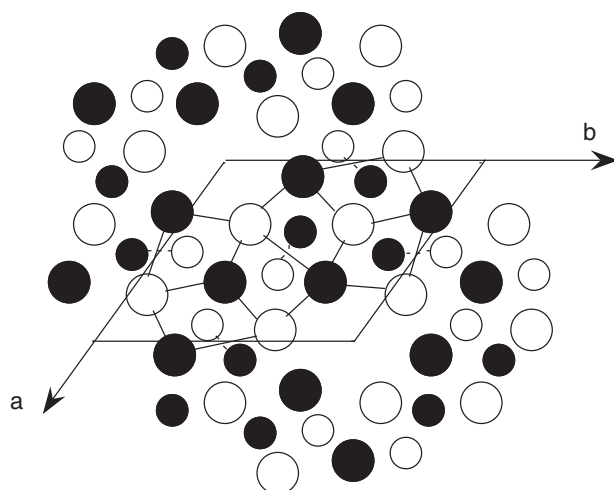
Measurements of the specific heat of  $\text{Hg}_x\text{Nb}_3\text{Te}_4$  with  $0 \leq x \leq 0.8$  are reported for the temperature range  $0.35 \leq T \leq 11$  K. The lattice contribution to the specific heat is adequately fitted by a combination of two Debye terms with the Debye temperatures  $\theta_D$  of about 15 and 105 K. The data are discussed in terms of several contributions to the Debye term with  $\theta_D = 15$  K: contributions made by CDW formation, Nb atoms displaced from their normal sites and inserted atoms. The bulk superconductivity in  $\text{Nb}_3\text{Te}_4$  has been observed by adding Hg, but only a small fraction of the material is superconducting. The electronic contribution  $\gamma T$  to the specific heat increases considerably with the addition of Hg. The increase in  $\gamma T$  is discussed in terms of a set of bands of electrons and holes.

## 1. Introduction

The crystal structure of the compound  $\text{Nb}_3\text{X}_4$  with  $\text{X} = \text{S}, \text{Se}, \text{Te}$  is characterized by the presence of metallic linear chains and large empty channels [1]. These structure features lead to highly anisotropic electrical properties [2–7], charge-density-wave (CDW) formation [8, 9] and the insertion of a large amount of metal atoms [10–14].

The structure of  $\text{Nb}_3\text{X}_4$  is hexagonal and its unit cell contains six Nb atoms and eight chalcogens [1, 15, 16], as shown in figure 1. Each Nb atom is surrounded by six chalcogens at the corner of a deformed octahedron of  $\text{NbX}_6$ . Each octahedron is linked to two other octahedra by common faces and to four octahedra by common edges. The Nb atoms are shifted from the centres of the octahedra in the direction of the faces sharing two edges with other octahedra. The distance between these shifted Nb atoms is 2.973 Å and is comparable to the corresponding value in Nb metal (2.859 Å). Thus zigzag Nb–Nb chains are formed along the  $c$  axis. Another remarkable feature of the  $\text{Nb}_3\text{X}_4$  structure is the presence of large empty channels along the  $c$  axis.

The electrical resistivity of  $\text{Nb}_3\text{X}_4$  with  $\text{X} = \text{S}$  and  $\text{Se}$  follows a  $T^3$  form below 80 K [2, 3]. Such temperature dependence of the resistivity can be explained on the basis of carrier–carrier



**Figure 1.** Crystal structure of  $\text{Nb}_3\text{Te}_4$  viewed along the  $c$  axis. Nb atoms are indicated by small circles and Te atoms by large circles. Atoms on the plane with  $z = c/4$  are drawn as full circles and ones on the plane with  $z = 3c/4$  as open circles. The unit cell is shown by full lines. Nb–Nb chains and octahedra of  $\text{NbTe}_6$  in the unit cell are shown by dotted and thin lines.

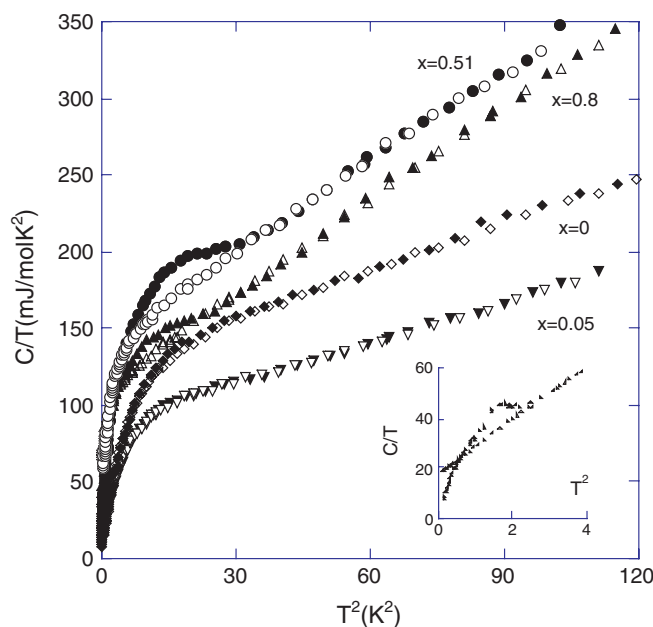
umklapp scattering in the quasi-one-dimensional energy band structure [17]. However,  $\text{Nb}_3\text{Te}_4$  shows two resistivity anomalies at 113 and 49 K [18]. The former is caused by CDW formation with commensurate wavevectors. With the addition of Hg, the CDW formation is enhanced at  $x \leq 0.03$  but it is suppressed at  $x > 0.03$ . The anomaly at 49 K is of unknown origin. However, since the magnitude of the anomalous resistivity is affected by the addition of Hg or In [4, 14], it appears that the anomaly is due to another CDW formation. The superconducting characteristic is also affected considerably by the addition of Hg: the superconducting transition temperature is increased from 1.8 to 5.2 K and the upper critical fields become highly anisotropic [4].

The energy band structure of  $\text{Nb}_3\text{S}_4$  is first calculated by Bullett [19] using an atomic-orbital method and that of  $\text{Nb}_3\text{X}_4$  is calculated by Oshiyama [17, 20] using the linear combination of atomic orbitals method. The Fermi surfaces of  $\text{Nb}_3\text{X}_4$  obtained by Oshiyama consist of warped plane-like sheets. The bandwidths along the chain directions are in the range of 1.5–2.5 eV and those along the interchain directions are of the order of 0.1 eV. The ratio of the bandwidth along the chain direction to that along the perpendicular direction is 15–19. For the band structure of  $\text{Nb}_3\text{S}_4$ , Canadell and Whangbo [21] have obtained similar results using a tight-binding approximation on the basis of the extended Hückel method and suggested that the Fermi surfaces and densities of states at the Fermi level of  $\text{Nb}_3\text{X}_4$  can be significantly modified by alkaline-metal intercalation.

In this paper we report on the specific heat of  $\text{Hg}_x\text{Nb}_3\text{Te}_4$  in the temperature range 0.35–11 K. Two of us previously reported on the specific-heat measurements of pure  $\text{Nb}_3\text{Te}_4$  [7], that the lattice specific heat of  $\text{Nb}_3\text{Te}_4$  indicates a  $T^3$  dependence below 2 K and in the range of 5–12 K. For such behaviour of the lattice specific heat, a satisfactory explanation was not given. The purpose of this work is to measure systematically the specific heats of  $\text{Nb}_3\text{Te}_4$  inserted with mercury to determine the nature of the non-usual Debye behaviour.

## 2. Experimental procedure

Specific-heat measurements were made using a thermal-relaxation method [22]. The measurement was carried out with no applied magnetic field and then a field of 6 T being

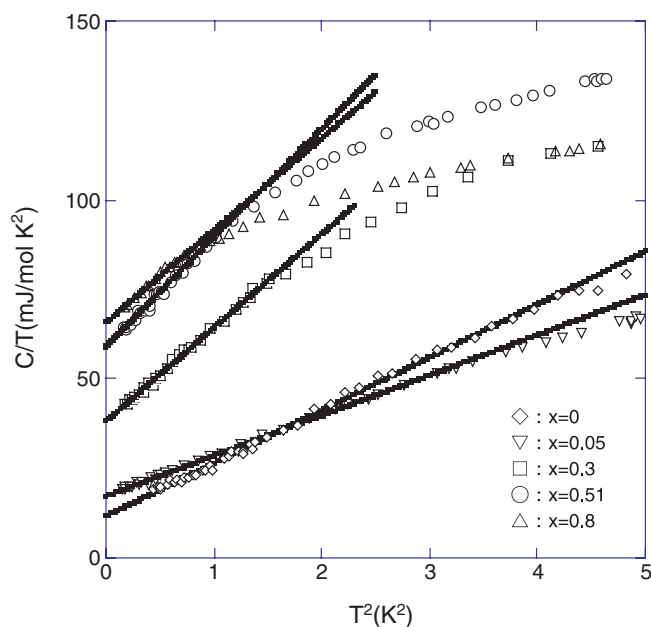


**Figure 2.** Specific heat of  $\text{Hg}_x\text{Nb}_3\text{Te}_4$  with  $x = 0, 0.05, 0.51$  and  $0.8$ . Full and open symbols are data in no applied field and in a field of 6 T. The inset shows the specific heats for  $x = 0.05$  at below 2 K.

applied perpendicular to the  $c$  axis. The magnitude of the upper critical field is  $H_{C2\perp}$ , for this direction is the smallest and is about 3 T at 0 K [4]. Several single crystals of total mass 60–80 mg were greased to a sapphire bolometer with the addenda contributing about 8% to the measured heat capacity. The specific heat of each sample at a given temperature was obtained by subtracting the heat capacity of the addenda (indium pads, thermometer and heater) from the gross heat capacity of the sample plus addenda. The temperature of the sample was measured by a ruthenium-oxide-resistance thermometer placed in close proximity. Single crystals of  $\text{Nb}_3\text{Te}_4$  were prepared by an iodine-vapour-transport method [23–25]. The grown crystals were always fibres, being elongated parallel to the  $c$  axis. For mercury insertion, Hg and single crystals of  $\text{Nb}_3\text{Te}_4$  in the desired molar ratio were sealed in an evacuated quartz tube. The tube was then kept at about 710 K for 10 days. The purity of Hg was 4N. If there was no residual Hg, the nominal value was used as the Hg concentration for a given compound.

### 3. Results

Figure 2 shows the specific heats  $C$  for  $x = 0, 0.05, 0.51$  and  $0.8$  plotted as  $C/T$  versus  $T^2$ , where the full and open symbols are data in a zero magnetic field and a field of 6 T, respectively. The major features of the specific heats are the large apparent linear term between 6 and 11 K and the unusual functional form of the temperature dependence below 5 K. In pure  $\text{Nb}_3\text{Te}_4$ , which becomes superconducting at 1.8 K ( $=T_{RC}$ ), an increase in the specific heat due to the superconducting transition has not been found down to 0.35 K. This fact agrees with the former determination [7]. The  $T_{RC}$  is a superconducting transition temperature determined by a resistivity method and is listed in table 1. With the addition of Hg, the specific heat of  $\text{Nb}_3\text{Te}_4$  in a zero field shows an increase at 1.6–5.6 K, depending upon the value of  $x$ . Since the



**Figure 3.** Specific heat in the normal state of  $\text{Hg}_x\text{Nb}_3\text{Te}_4$  with  $x = 0, 0.05, 0.3, 0.51$  and  $0.8$  below  $2.2$  K. The full line is the least-squares fit to data given by  $C = \gamma T + bT^3$ .

**Table 1.** Fundamental parameters in the model of two Debye terms.

$x$	$\beta_L$ ( $\text{mJ mol}^{-1} \text{K}^{-4}$ )	$\beta_H$ ( $\text{mJ mol}^{-1} \text{K}^{-4}$ )	$\theta_{DL}$ (K)	$\theta_{DH}$ (K)	$b$	$T_{RC}$ (K) <sup>a</sup>
0	14.8	0.981	18	112	0.037	1.8
0.05	11.3	0.849	16	120	0.021	2.8
0.1	13.7	1.34	14	104	0.017	4.0
0.3	26.2	1.77	13	94	0.023	5.2
0.51	30.4	2.02	12	92	0.018	5.2
0.8	25.7	2.03	11	94	0.01	

<sup>a</sup> Estimated value from figure 5 in [4].

increase for  $x = 0.05$  is not clear in figure 2, the specific heat is shown in the inset.  $\text{Hg}_x\text{Nb}_3\text{Te}_4$  with  $x = 0.05$  shows a sharp increase in the specific heat, but  $x > 0.05$  shows widely varying amounts of excess specific heat.

The specific heat in the normal state at temperatures below  $2$  K can be well fitted by the following relation:

$$C/T = \gamma + \beta_L T^2, \quad (1)$$

as shown by the full lines in figure 3. The temperature range over which the data are linear on this plot decreases with increasing Hg concentration. The values of  $\gamma$  and  $\beta_L$  for  $x = 0$  obtained by the least-squares fit to this equation are  $\gamma = 11.9 \text{ mJ mol}^{-1} \text{K}^{-2}$  and  $\beta_L = 14.8 \text{ mJ mol}^{-1} \text{K}^{-4}$ . The  $x$  dependence of  $\gamma$  is shown in figure 4. The magnitude of  $\gamma$  increases in proportion to the value of  $x$  up to about  $x = 0.5$  and thereafter increases gradually.

Figure 5 shows the excess specific heats  $\Delta C$  for  $x = 0.05, 0.1, 0.3, 0.51$  and  $0.8$  plotted as  $\Delta C/\gamma T$  versus  $T$ , where  $\Delta C$  is the difference between the specific heats in a zero field and an applied field of  $6$  T. The  $x$  dependence of  $\Delta C$  has the following characteristics. The

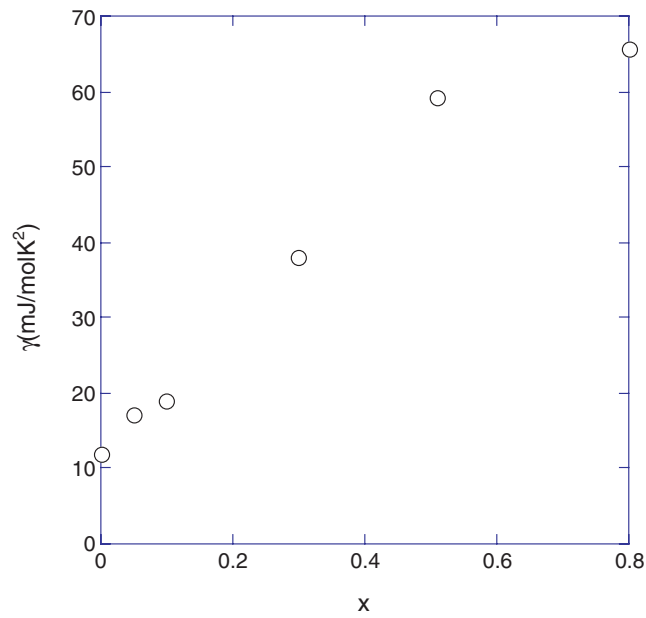


Figure 4. Hg concentration dependence of  $\gamma$  in  $\text{Hg}_x\text{Nb}_3\text{Te}_4$ .

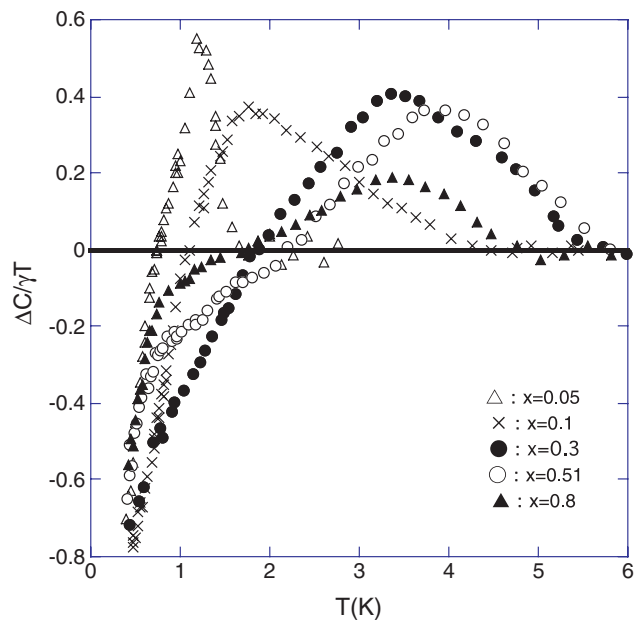


Figure 5. Temperature dependence of the excess specific heat  $\Delta C$  for  $x = 0.05, 0.1, 0.3, 0.51$  and  $0.8$ .

rise temperature at which  $\Delta C$  appears is lower than  $T_{\text{RC}}$  at low concentrations of about  $x = 0.05$ , but it approaches  $T_{\text{RC}}$  with increasing Hg concentration. The magnitude of  $\Delta C/\gamma T$  at high concentrations of  $x = 0.8$  is small compared to that of intermediate concentrations of  $x = 0.3\text{--}0.5$ .

#### 4. Discussion

The experimental value of  $\gamma$  is proportional to  $(1 + \lambda)D(\varepsilon_F)$ , where  $\lambda$  is the electron–phonon enhancement factor and  $D(\varepsilon_F)$  electronic density of states at the Fermi level. For  $\text{Nb}_3\text{Te}_4$ , since the value of  $D(\varepsilon_F)$  assuming  $\lambda = 0$  is already obtained by a band-structure calculation [17], we may calculate  $\lambda$  and obtain  $\lambda = 0.1$ . The value of  $\lambda = 0.1$  is less than 0.55 of  $\text{Nb}_3\text{S}_4$  [5], which is isomorphous with  $\text{Nb}_3\text{Te}_4$  and does not show a phase transition, whereas  $\text{Nb}_3\text{Te}_4$  undergoes a phase transition at 113 K and possibly at 49 K, as mentioned above. The CDW formation reduces  $D(\varepsilon_F)$  and the ratio of the reduction of  $D(\varepsilon_F)$  to that in the absence of the CDW formation is about 20% [26]. If we take such a factor into account, the magnitude of  $\lambda$  becomes 0.34. This value is close to that of  $\text{Nb}_3\text{S}_4$ . Hence, the result indicates that the linear term  $\gamma T$  at temperatures below 2 K in figure 3 is caused by electronic contribution to the specific heat.

Now we consider the lattice specific heat  $C_L (=C - \gamma T)$ . The Debye model correctly describes the lattice specific heat of all solids at low temperatures and gives a  $T^3$  dependence of the specific heat. The  $C_L$  of  $\text{Hg}_x\text{Nb}_3\text{Te}_4$  shows a  $T^3$  dependence at temperatures below 2 K and above 5 K. The crystal structure of  $\text{Nb}_3\text{Te}_4$  consists of Nb chains running along the  $c$  axis with the metallic distance between Nb atoms on the chain, but the interchain distance exceeds the metallic distance as described above. Hence, considering electronic properties,  $\text{Nb}_3\text{Te}_4$  may be regarded as an aggregate of one-dimensional lattices. However, if considered from the standpoint of lattice vibrations, this material should be regarded as a three-dimensional lattice. Hence, we assume the superposition of two Debye terms, being expressed as follows:

$$C_L = bC_L(\theta_{DL}) + C_H(\theta_{DH}), \quad (2)$$

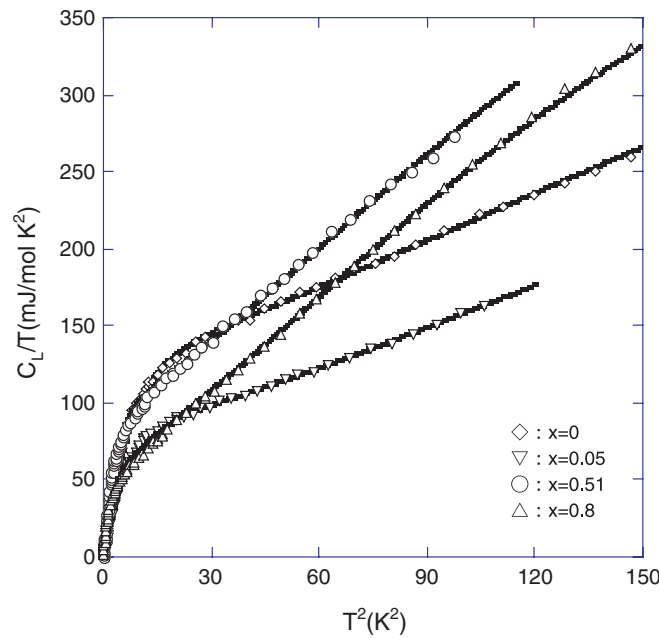
where  $C_L$  and  $C_H$  are the usual three-dimensional Debye terms with the Debye temperatures  $\theta_{DL}$  and  $\theta_{DH}$ , and  $b$  is a free parameter. In  $\text{Nb}_3\text{Te}_4$ , there will be 21 branches to the phonon-dispersion relation: three acoustical branches and the others optical. Since the specific heat is measured at low temperatures, only the acoustical branches contribute to the specific heat.

In figure 6, we show the typical results of this expression using the experimental data. The lattice specific heat is determined by two characteristic Debye temperatures:  $\theta_{DL}$  and  $\theta_{DH}$ , and the parameter  $b$ . A certain degree of approximation for  $\theta_{DL}$  and  $\theta_{DH}$  may be obtained from the slope  $\beta_i$  of the  $C_L/T$  versus  $T^2$  plot at temperatures below 2 K and above 5 K, using the relation  $\beta_i = 1944/\theta_i^3$  ( $i = L$  or  $H$ ). The full curves in figure 6 are the values of  $C_L$  calculated using the optimum values of  $\theta_{DL}$ ,  $\theta_{DH}$  and  $b$ . The parameters obtained for various values of  $x$  are shown in table 1. On the whole, these parameters decrease gradually with increasing Hg concentration. The agreement between the experimental results and the analysis provides proof that the unusual specific heat of  $\text{Hg}_x\text{Nb}_3\text{Te}_4$  results from the excitations of some low-frequency three-dimensional modes, in addition to the usual three-dimensional modes.

The crystal structures of  $\text{Nb}_3\text{S}_4$  and  $\text{Nb}_3\text{Se}_4$  are isomorphous with that of  $\text{Nb}_3\text{Te}_4$  as mentioned above. The main differences in electrical and thermal properties between the first two and  $\text{Nb}_3\text{Te}_4$  are as follows:

- (i) Both  $\text{Nb}_3\text{S}_4$  and  $\text{Nb}_3\text{Se}_4$  show no CDW formation.
- (ii) The residual resistivity ratio  $\rho_{300}/\rho_{4.2}$ , which is the ratio of the resistivity at 300 K to that at 4.2 K along the  $c$  axis, is 80–170 for  $\text{Nb}_3\text{S}_4$  and  $\text{Nb}_3\text{Se}_4$  [2, 3] and about 5 for  $\text{Nb}_3\text{Te}_4$ , being not greatly affected by the addition of impurities [4, 25].
- (iii) The lattice specific heats of  $\text{Nb}_3\text{S}_4$  and  $\text{Nb}_3\text{Se}_4$  are described satisfactorily by a cubic Debye law up to 7–13 K [27].

Accordingly, two possible mechanisms can be considered for the origin of the Debye term with  $\theta_{DL}$ . One is that the Debye term is caused by the CDW transition. However, although



**Figure 6.** Lattice specific heat  $C_L$  of  $\text{Hg}_x\text{Nb}_3\text{Te}_4$  with  $x = 0, 0.05, 0.3, 0.51$  and  $0.8$ . Open symbols are experimental data. Full lines are lattice specific heats calculated using the superposition of two Debye terms.

the resistivity anomaly due to the CDW formation disappears at  $x \geq 0.3$  [4], the unusual temperature dependence of the specific heat in  $\text{Hg}_x\text{Nb}_3\text{Te}_4$  is still present up to  $x = 0.8$ . For this reason, this mechanism is not reasonable.

The other is as follows. The fact that the value of  $\rho_{300}/\rho_{4.2}$  for  $\text{Nb}_3\text{Te}_4$  is small and is not greatly affected by impurities indicates that impurity atoms are inserted into the void channels and the electric current mainly flows on the Nb chain. Then, the residual resistivity should mainly arise from imperfections of the Nb chains which form barriers for electronic transport. The imperfections would be caused by the displacement of Nb atoms from their normal lattice sites into the empty channels, interstitial positions or onto the wrong lattice sites. In  $\text{Nb}_3\text{Te}_4$ , it appears that the greater part of the displaced Nb atoms has moved away from their lattice positions into the empty channels. The displaced or inserted atoms would contribute to the specific heat in the following manner:

- (i) If all the atoms vibrate independently of one another with the same frequency, they contribute to the specific heat as an Einstein mode. As a result, since the number of atoms in the channels increases with increasing Hg concentration, the specific heat will also increase with increasing Hg concentration. However, the experimental result suggests that the specific heat due to an Einstein mode has not been observed.
- (ii) When there are enough displaced Nb atoms or inserted Hg atoms, they will interact with each other and there may be lower frequency modes.
- (iii) If the atoms in the channels are strongly coupled to the host lattice, they would contribute to the specific heat as a Debye term with  $\theta_{\text{DH}}$ .

The decrease in the value of  $b$  in equation (2) by the addition of Hg suggests that the inserted atoms are strongly coupled to the host lattice, because the atomic radius for Hg is of the same order of magnitude as for the void channel. At present, since we have no information about the



distribution of impurity atoms in the void channels, we cannot identify the origin of the Debye term with  $\theta_{DL}$ . Therefore, the exact structure of the Debye term with  $\theta_{DL}$  is not known but it seems that the atoms displaced or inserted into the void channels play an important role in the Debye term with  $\theta_{DL}$ . With the addition of Hg, the slight decrease in  $\theta_{DL}$  and  $\theta_{DH}$ , except near  $x = 0.05$ , is most probably due to the slight increase in the lattice constants.

We now consider the prominent increase in  $\gamma$  by the addition of Hg. This increase would be described as basically electronic in origin and the following mechanisms can be considered which lead to the increase in  $\gamma$ : strong electron–phonon coupling and the existence of a large structure in the electronic density of states near the Fermi level. The thermoelectric power of  $\text{Hg}_x\text{Nb}_3\text{Te}_4$  indicates that the conduction band of  $\text{Nb}_3\text{Te}_4$  consists of a set of bands of electrons and holes, with the dominant carriers changing from electrons to holes with increasing Hg concentration [4]. In such a case,  $\gamma$  is the sum of the contributions from each band:  $\gamma_i \propto (1 + \lambda_i)D_i(\varepsilon_{Fi})$ , where subscript  $i$  denotes  $i = e$  for electrons or  $i = p$  for holes. The presence of superconductivity in  $\text{Hg}_x\text{Nb}_3\text{Te}_4$  provides the value of  $\lambda$ . We can find it from the McMillan formula [28] if the Debye temperature  $\theta_D$ , the superconducting transition temperature  $T_C$  and the Coulomb repulsive constant  $\mu^*$  are known. Since the dominant carriers are electrons for  $x < 0.3$  and holes for  $x \geq 0.51$  below 10 K [4], we are able to assume that  $\gamma \propto (1 + \lambda_e)D_e(\varepsilon_{Fe})$  for  $x = 0$  and  $\gamma \propto (1 + \lambda_p)D_p(\varepsilon_{Fp})$  for  $x = 0.51$  and obtain that  $\lambda_e = 0.58$  for  $x = 0$  and  $\lambda_p = 0.99$  for  $x = 0.51$ , where we have used  $\theta_D = \theta_{DH}$ ,  $T_C = T_{RC}$  and assumed  $\mu^* = 0.1$ . The result suggests that, since the magnitude of  $\lambda$  for holes is of the same order as for electrons, the increase in  $\gamma$  cannot be explained by this mechanism. The result of the calculation of the energy band structure in  $\text{Nb}_3\text{Te}_4$  indicates that there is no large density of states near the Fermi level for electrons [17]. For the above reasons, although there is no information for the density of states of holes at present, in order to explain the remarkable increase in  $\gamma$  it is required that holes have much greater  $D_p(\varepsilon_{Fp})$  than electrons. Since the density of electronic states is proportional to the density of states of effective mass  $m_d$ , holes probably have a remarkably greater  $m_d$  than that of electrons. This is supported by the fact that the anisotropy of the upper-critical field for holes is considerably larger than that for electrons [4]. As a result, it appears that the increase in  $\gamma$  by the addition of Hg occurs due to the large density of states of effective mass of the holes.

One of the prominent observations in our experiment is the appearance of excess specific heat. Since specific-heat measurements detect only true bulk superconductivity, the excess specific heat is due to this superconductivity. The magnitude of the excess specific heat increases up to about  $x = 0.5$ , but above this concentration it drops steeply. Such a behaviour of excess specific heat can be interpreted as follows. Since pure  $\text{Nb}_3\text{Te}_4$  shows no trace of bulk superconductivity,  $\text{Nb}_3\text{Te}_4$  itself is a filamentary superconductor. This filamentary superconductivity would be attributable to the fact that the electric current mainly flows on the Nb chains and the interaction between Nb chains is negligibly weak. With the addition of Hg, a tiny fraction of the interactions is probably enhanced and this enhancement leads to bulk superconductivity. Since the radius of the Hg ion is comparable to that of the void channel, the lattice of  $\text{Nb}_3\text{Te}_4$  would be distorted by the inserted atoms. This lattice distortion would lead to enhancement of the coupling for certain concentrations of Hg. However, with the addition of Hg, the lattice constants are simultaneously increased and this suppresses the coupling. In the case where the enhancement outweighs the suppression, the superconducting fraction will be increased. The reverse also applies in some cases. The increase in the excess specific heat at  $x \leq 0.51$  corresponds to the former case and the decrease at  $x > 0.51$  corresponds to the latter case.

In summary, in the specific heat of  $\text{Hg}_x\text{Nb}_3\text{Te}_4$ , we have observed an unusual change in functional form below 5 K. Such behaviour of the specific heat can be explained well

by the sum of two Debye terms with the Debye temperatures of about 15 and 105 K. The magnitude of  $\gamma$  increases considerably with the addition of Hg. The increase in  $\gamma$  would be caused by the increase in the contribution of holes with a large density of states of effective mass to the electronic specific heat. Although pure  $\text{Nb}_3\text{Te}_4$  does not show any trace of bulk superconductivity, a small fraction of  $\text{Nb}_3\text{Te}_4$  shows bulk superconductivity by the addition of Hg. The bulk superconductivity is probably caused by the enhancement of interactions between Nb chains due to the lattice distortion by inserted Hg atoms.

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