Coexistence of Superconductivity and CDWs in $Nb_{1-x}Ta_xSe_3$

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Abstract

The superconducting transition temperature T_c and the sizes of the resistive anomalies due to both q_1- and q_2-CDW formations were examined in single crystals of $Nb_{1-x}Ta_xSe_3$. As Ta-concentration increases the sizes of the resistive anomalies decrease but that due to the q_1-CDW begins to increase at 5 at%. On the contrary, Tc initially increases but it also turns to decrease at the same concentration. The results are discussed in terms of the correlation between superconductivity and CDWs.

$NbSe_3$ undergoes two CDW transitions (q_1- and q_2-CDW) at 142K and 58K, which are associated with highly anisotropic electronic energy bands. Electron and X-ray diffraction studies showed that both CDWs are incommensurate with the underlying lattice[1,2] and independent of each other[3]. At low temperature this compound becomes superconductive when applied pressure[4,5] or doped with impurities[6,7]. Monceau et al.[4] tried to explain the enhancement of the superconducting transition temperature Tc under pressure in terms of the semimetallic band structure of $NbSe_3$[8]. On the other hand, Fuller et al.[6] proposed that Tc is enhanced through the suppression of the q_2-CDW under pressure. However pressure dependences of Tc, which were obtained by the resistive[5] and by the diamagnetic measurements[4], were inconsistent with each other. Two possible reasons for the inconsistency can be considered; one is in the technical difficulty in high pressure experiments and another is a resistive drop around 2K due to the extrinsic superconductivity observed in an agglomerate of single crystals even at ambient pressure. This extrinsic superconductivity was found to be associated with crystal boundaries.[9]

No reliable result has been obtained in the doping studies because the extrinsic superconductivity has not been separated. In the present study, superconductivity and both q_1- and q_2-CDW formations were examined in $NbSe_3$ doped with isoelectronic impurity Ta. Single crystals were used in order to exclude the extrinsic superconductivity. The correlation between superconductivity and both CDW formations is discussed. Preliminary results have been reported elsewhere.[10]

Crystals of $Nb_{1-x}Ta_xSe_3$ were grown by heating stoichiometric proportions of $Nb_{1-x}Ta_x$ alloys and Se in quartz tube for 2 weeks at 700°C. Starting material Nb contains 200 ppm of Ta. Doped crystals were prepared within 8 at% of Ta. Any change of crystal symmetry could not be detected in $Nb_{0.92}Ta_{0.08}Se_3$ by the X-ray Weissenberg method. As Ta-concentration the nominal value was used because no scatter was found in the resistive anomalies due to both CDW formations nor Tc within a given batch. The resistivity along the b-axis was measured by the usual four-probe dc method, down to 70mK. The low temperature was achieved in either a ^{3}He cryostat or a dilution refrigerator.

The resistive behaviors at low temperatures of both non-doped and doped crystals are shown in Fig. 1-a. The non-doped crystals do not show any drop of the resistivity at least down to 70mK but crystals do when doped with a small amount of Ta. The resistive transition curve in single crystals $Nb_{1-x}Ta_xSe_3$ is sharp, in contrast with the extrinsic superconductivity whose transition width is larger than 1K. In Fig. 1-b, T_c is plotted as a function of Ta-concentration, where T_c is conventionally defined as the midpoint of the resistive transition curve. T_c increases very steeply with an addition of Ta but begins to decrease gradually when Ta-concentration exceeds 5 at%.

The temperature dependence of the resistivity up to 300K is shown in Fig. 2. Two distinct resistive anomalies due to the q_1- and the q_2-CDW formations are seen in non-doped crystal but these anomalies become very broad with the addition of a small amount of Ta. As the result, the CDW transition temperatures in doped crystals can be no longer determined. Then we investigated the size of the resistive anomalies due to the CDW formations which is proportional to the area of the Fermi surface (FS) destructed by the CDW formation. To define the size of the resistive anomaly, we used the α parameter given by

$$\alpha = (R_1 - R_2) / R_1 = (\sigma_2 - \sigma_1) / \sigma_2 ,$$

where R_1 (σ_1) is the peak resistance (conductivity) in the resistive anomaly and R_2 (σ_2) is the resistivity(conductivity) which is expected in the absence of the CDW transition, as shown in Fig. 2. The α parameter was first introduced by Ong et al.[11] and by Nishida et al.[12] for non-doped crystal. The conductivity of metal is given by $\sigma = Ne^2 v_F{}^2 \tau/3$ where N, v_F and τ are the density of states at the Fermi level E_f, the Fermi velocity and the relaxation time of conduction electrons respectively. Using N and ΔN (the reduction of N due to the CDW formation), α can be written by

$$\alpha = (\sigma_2 - \sigma_1) / \sigma_2 = (N - (N - \Delta N)) / N = \Delta N / N ,$$

if only the density of states at E_f is affected by the CDW formation. Then the α parameter gives the quantity $\Delta N/N$, that is, the ratio of the portion of FS destroyed by the CDW gap to the whole FS before the gap forms. The values of α obtained in non-doped crystal are in reasonable agreement with those of $\Delta N/N$ determined from the calorimetric[13], the diamagnetic[14] and the NMR studies[15].

In Fig. 3, the parameters α_1 and α_2 for the q_1- and the q_2-CDW transitions respectively were plotted, together with T_c, as functions of Ta-concentration. The quantity α_2 decreases monotonously to zero with the addition of Ta while α_1 first decreases slightly but begins to increase at 5 at%. It is noticeable that T_c turns to decreasing gradually at the same concentration 5 at%. These facts mean that the concentration dependence of T_c correlates with those of α_1 and α_2.

There are several sheets of FS in $NbSe_3$. Some sheets of

FS have planar portions; electrons on these portions have one-dimensional (1-D) characteristics. The q_1- and the q_2-CDW formations open the gaps over planar portions on two different pairs of sheets.[8] The values of α_1 and α_2 are proportional to the areas of FS destroyed by each CDW gap respectively. The remnant portions of FS after the CDW gaps form are expected to contribute to superconductivity. In general, the shape of FS will be modified to a certain extent by doping. In some case, the area of the 1-D portion on FS will decrease with an addition of impurity and the CDW formation is suppressed. If the total area of FS is less affected by doping, the remnant area after the CDW formations increases and Tc increases. The situation below 5 at% in the present study is expected to correspond to this case, where T_c increases steeply while both α_1 and α_2 decrease. In another case, the portion of 1-D characteristics on FS will increase by doping. The CDW formation is enhanced and T_c is lowered. Above 5 at% T_c decreases with Ta-concentration. The decrease of the remnant FS due to the enhancement of the q_1-CDW is considered to overcome the increase of that due to the suppression of the q_2-CDW in this regime.

The above speculation is supported by the following simple calculation of the Ta-concentration dependence of T_c. Taking into consideration that the q_2-CDW opens the gap over the portion α_2 of the remaining FS after the q_1-CDW gap forms, the density of states N_s at E_f after both q_1- and q_2-CDW formations can be estimated as

$$N_s = N_{total} - \Delta N = N_{total} - N_{total}(\alpha_1 + (1-\alpha_1)\alpha_2),$$

where N_{total} is the total density of states at E_f and ΔN is the reduction of N due to both CDW formations. T_c is calculated by using N_s estimated as above and the isotropic and weak coupling BCS theory

$$T_c = 0.85\theta_D \exp(-1/N_s V),$$

where θ_D is the Debye temperature, V is the electron-phonon coupling constant. N_{total}, V and θ_D are assumed to be little affected by doping a small amount of Ta, since impurity Ta is isoelectronic and no change of crystal symmetry due to doping could be observed. The calorimetric study gives 140K for θ_D of non-doped crystal.[16)] $N_{total}V$ was determined to obtain the best fitting between the calculated result and the observed one. The best result was obtained for $N_{total}V = 0.42$, as shown in Fig. 1-b. The obtained result reproduces the essential features of the observed one.

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Figure Captions

Fig.1. a) Low temperature resistivity of Ta-doped $NbSe_3$.
b) The superconducting transition temperature T_c as a function of Ta-concentration. The broken line is the calculated one (see in text).

Fig.2. Examples of the normalized resistivity R(T)/R(300K) as a function of temperature. Inlet; schematic definition for R_1 and R_2.

Fig.3. The sizes (α_1 and α_2) of the resistive anomalies due to q_1- and q_2-CDW formations as functions of Ta-concentration. Broken line; T_c.

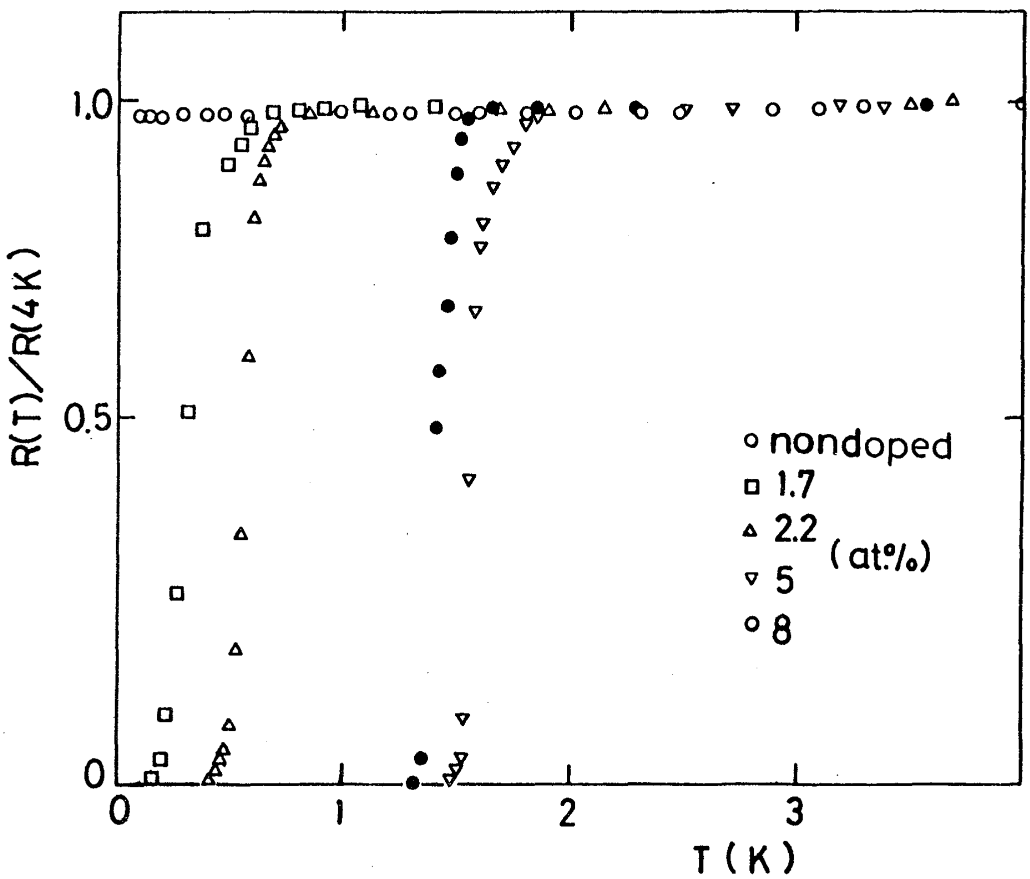

Fig 1-a

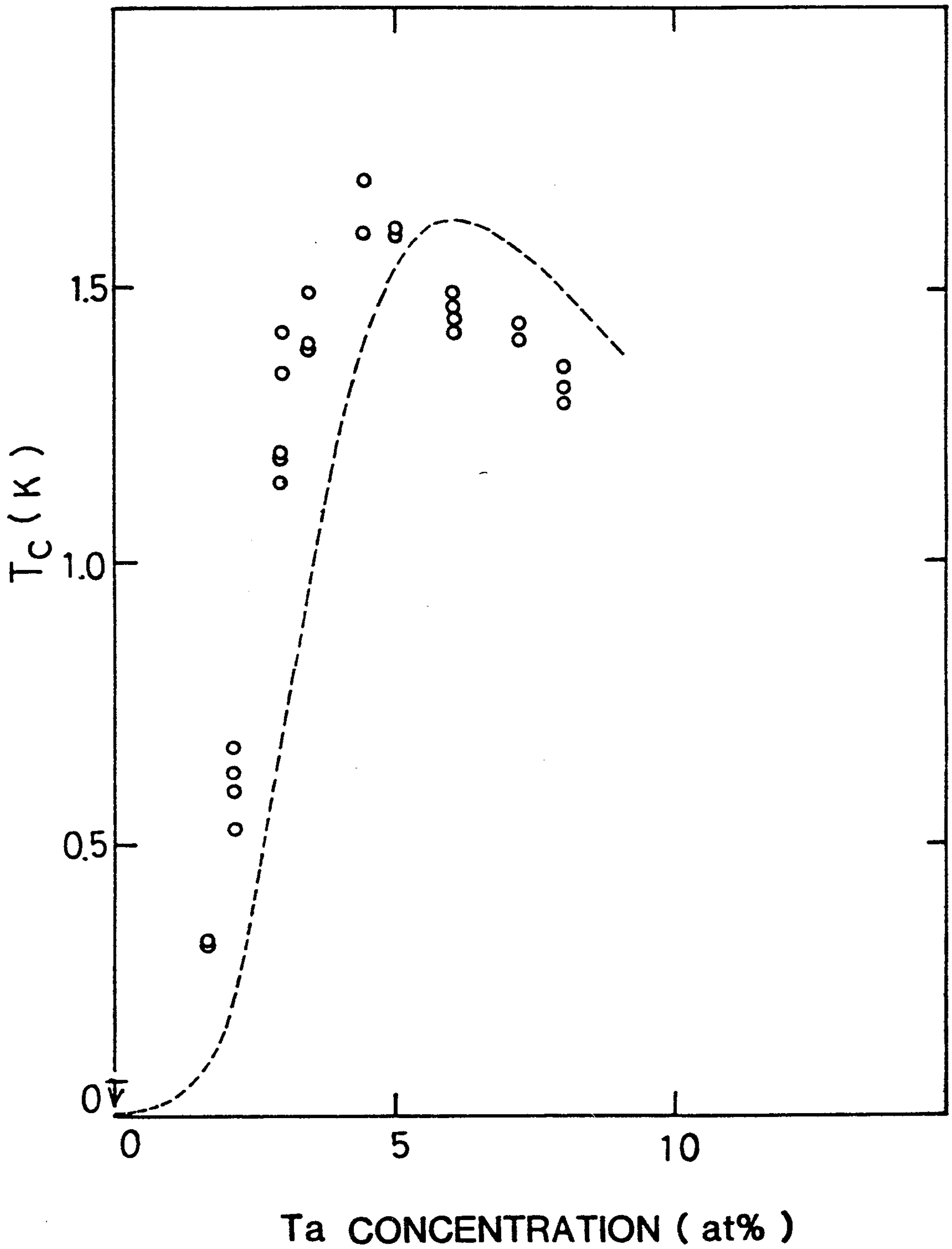

Fig 1-b

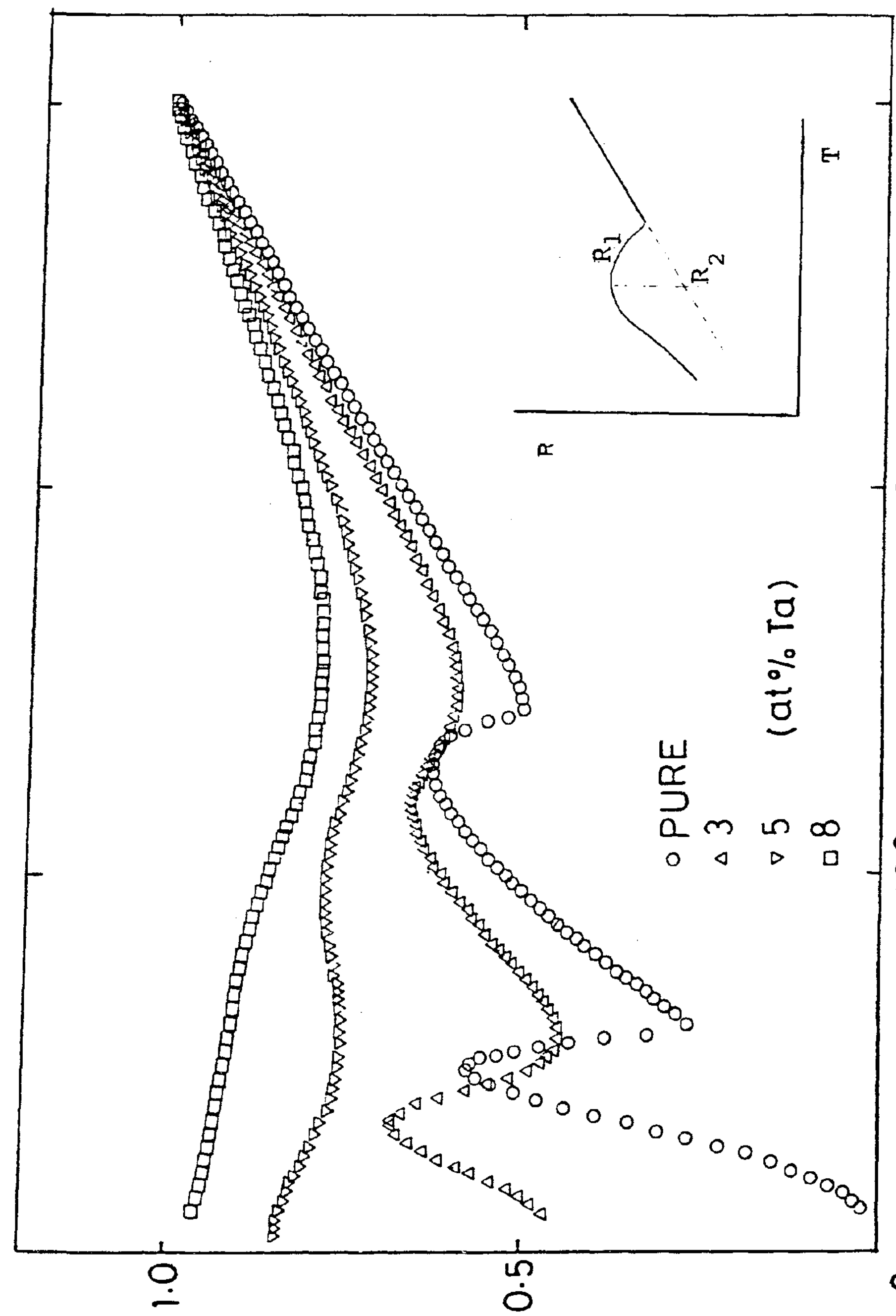

Fig 2

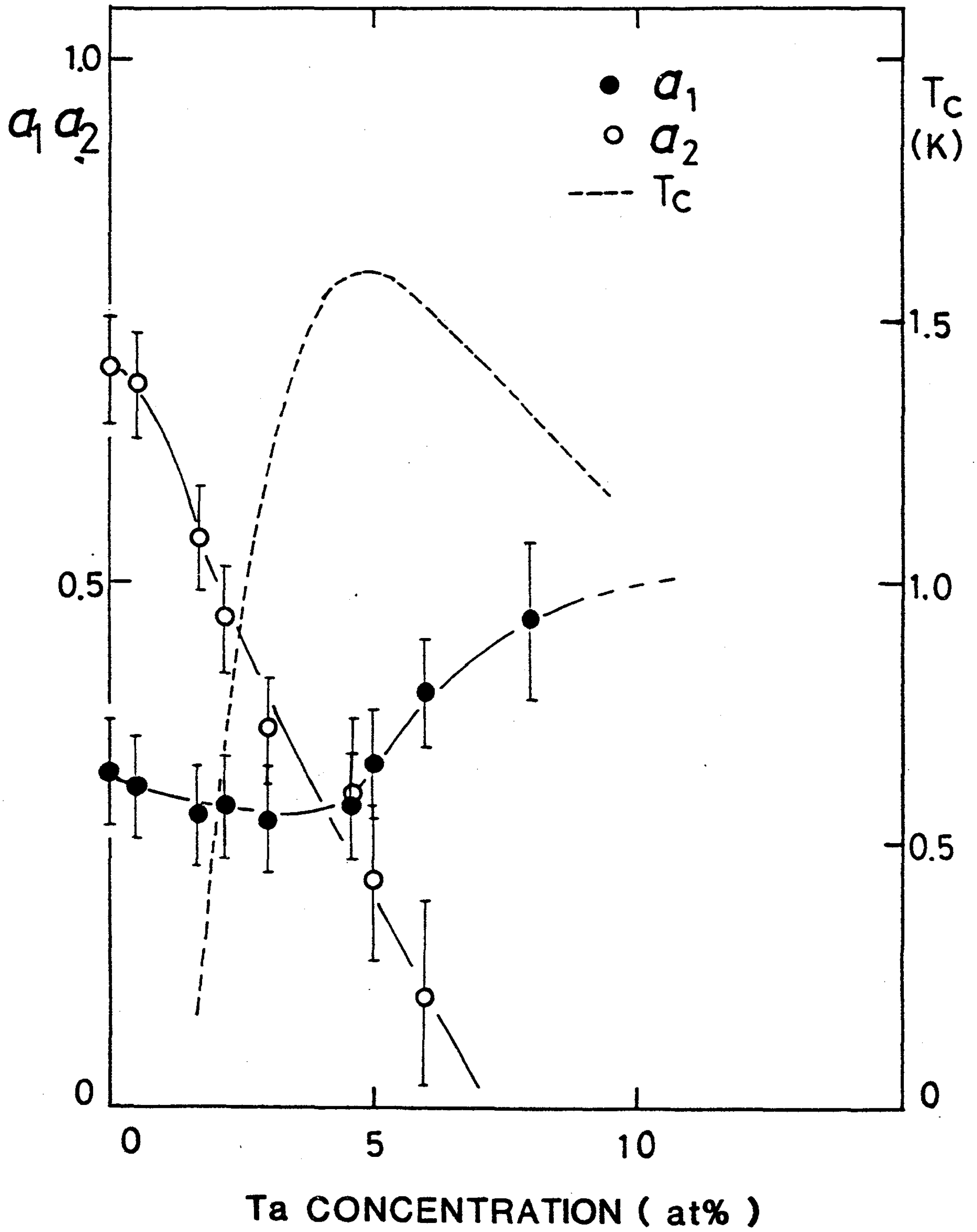

Fig 3