Electrical resistivity of polycrystalline niobium nitride films

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(Received 31 July 1987)

The electrical resistivity of magnetron-sputtered polycrystalline NbN thin films has been measured as a function of the temperature for a variety of samples exhibiting different grain structures. The data are very well described by a model recently proposed by Reiss, Vancea, and Hoffman for granular metallic systems. The model correctly predicts the observed negative temperature coefficient of resistivity and the occurrence of a minimum in the temperature dependence of the resistivity.

INTRODUCTION

Niobium nitride (NbN) is one of the leading materials in superconducting applications (critical temperature $T_c = 17$ K) and its properties have been extensively studied in this context. As indicated by electron-microscopy studies,[1,2] NbN films are generally polycrystalline with grains surrounded by voids or very disordered intergranular regions.

In contrast with other isostructural compounds,[3] very high normal-state resistivities[4] (often higher than the "metallic limit"), low residual resistivity ratios, negative temperature coefficient of resistivity (TCR), or minima in the resistivity as a function of the temperature have been reported for NbN and related to this granular structure.

The picture that is generally given to explain the anomalous behavior of the electrical resistivity in NbN is that of thermally activated hopping or tunneling occurring between rather low-resistivity grains separated by a nonconducting medium.[4]

In the present work we show how a simple model recently proposed for the electrical resistivity of polycrystalline samples[5] describes very well our experimental results on NbN sputtered films. Some general implications of our results will be also discussed.

THEORY

In a recent paper Reiss, Vancea, and Hoffman[5] put on theoretical ground the observation that, in a polycrystalline sample, the conductivity σ depends on the number of grains per mean free path, l_∞/D, in the following way:

$$\sigma = \frac{ne^2 l_\infty}{mv_F} G(l_\infty/D, \Gamma) , \tag{1}$$

where l_∞ is the innercrystalline mean free path describing the volume scattering of the electrons, D is the mean grain dimension, Γ is the mean probability for electrons to pass a grain boundary, n is the effective carrier concentration, m is the effective mass, and v_F the Fermi velocity.

In Ref. 5 the authors give an expression for the function $G(l_\infty/D, \Gamma)$ and show that it is well approximated by the empirical expression

$$G(l_\infty/D, \Gamma) = \Gamma^{l_\infty/D} , \tag{2}$$

already proposed by Hoffman and co-workers on the basis of the analysis of a number of experiments.[6]

From Eqs. (1) and (2) we can write

$$\rho(T) = \rho_\infty(T) \exp[AK/D\rho_\infty(T)] , \tag{3}$$

where $\rho(T) = 1/\sigma$ is the sample electrical resistivity, $A = -\ln\Gamma$, $K = mv_F/ne^2$, and $\rho_\infty(T) = K/l_\infty$.

The quantity K is fairly temperature independent, being only connected to electronic band-structure properties. The function $\rho_\infty(T)$ represents the temperature-dependent innercrystalline resistivity and for $A \to 0$ ($\Gamma \to 1$) or $D \to \infty$ we expect to find $\rho(T) \equiv \rho_\infty(T)$.

According to Eq. (3) a negative TCR ("nonmetallic" behavior) simply occurs when the condition $\rho_\infty(T) < AK/D$ ($l_\infty > D/A$) is satisfied, independently of the specific coupling mechanism between the grains (hopping, tunneling, or other), and can also occur if a temperature-independent transmission probability through the grain boundaries is assumed ($A = -\ln\Gamma = \text{const}$).

EXPERIMENTAL RESULTS AND DISCUSSION

As discussed in the Introduction, NbN seems to be an ideal system to check the validity of Eq. (3) and the ideas behind it. With this in mind, in our laboratory we have performed a systematic study of the electrical resistivity of sputtered films of this material.

The NbN films, 4000 to 6000 Å thick, were deposited by reactive magnetron sputtering using a triode configuration on sapphire substrates held at 600 °C. The details of the fabrication technique and the superconducting properties of the films are described elsewhere.[7]

All the films considered in the present work have $T_c > 14$ K, implying that the grains are close to stochiometry, but show different grain sizes and/or different

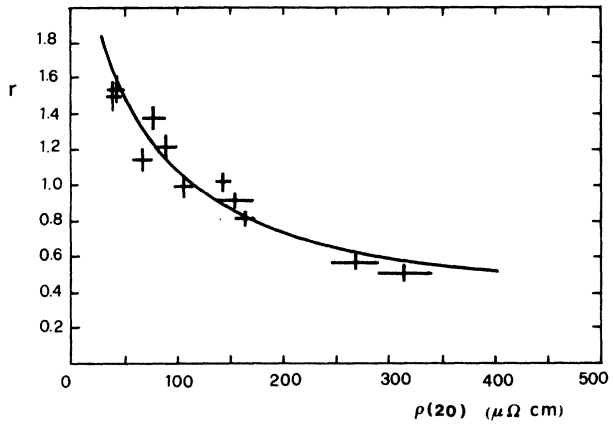

FIG. 1. Residual resistivity ratio r as a function of the low-temperature (residual) resistivity $\rho(20\ \mathrm{K})$. The continuous line represents the theoretical prediction [Eq. (4)], assuming $r_\infty = 2.2$ and $\rho_\infty(20\ \mathrm{K}) = 26\ \mu\Omega\,\mathrm{cm}$.

grain boundaries depending on the details of the deposition conditions.

In Fig. 1 the residual resistivity ratio, defined here as $r = \rho(300\ \mathrm{K})/\rho(20\ \mathrm{K})$ is reported as a function of the low-temperature resistivity $\rho(20\ \mathrm{K})$. The data points corresponding to $r < 1$ roughly correspond to films exhibiting a negative TCR.

From Eq. (3) we can easily write the following relation:

$$\frac{r}{r_\infty} = \left[\frac{\rho(20\ \mathrm{K})}{\rho_\infty(20\ \mathrm{K})}\right]^{1/r_\infty - 1}, \tag{4}$$

where we have defined $r_\infty = \rho_\infty(300\ \mathrm{K})/\rho_\infty(20\ \mathrm{K})$.

Equation (4) is plotted in Fig. 1 (continuous line) for $r_\infty = 2.2$ and $\rho_\infty(20\ \mathrm{K}) = 26\ \mu\Omega\,\mathrm{cm}$. The agreement between experiments and theory is very good and proves also that for all films we get essentially the same intragrain resistivity. The rather high value that we obtain for the intragrain room-temperature resistivity

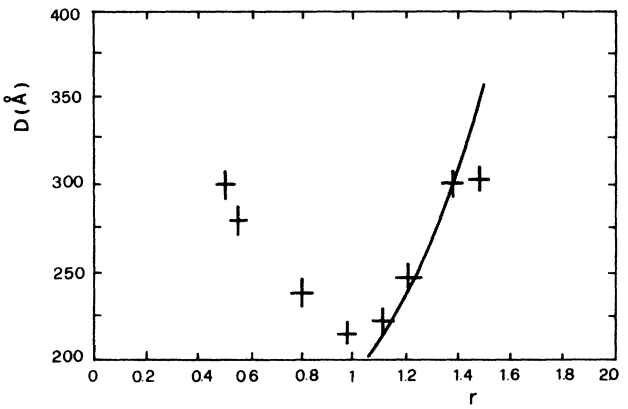

FIG. 2. Average grain size D as a function of the residual resistivity ratio r. The continuous line represents the theoretical prediction [Eq. (5)], assuming $r_\infty = 2.2$, $\rho_\infty(20\ \mathrm{K}) = 26\ \mu\Omega\,\mathrm{cm}$, and $AK = 7\times10^{-5}\ \mu\Omega\,\mathrm{cm}^2$.

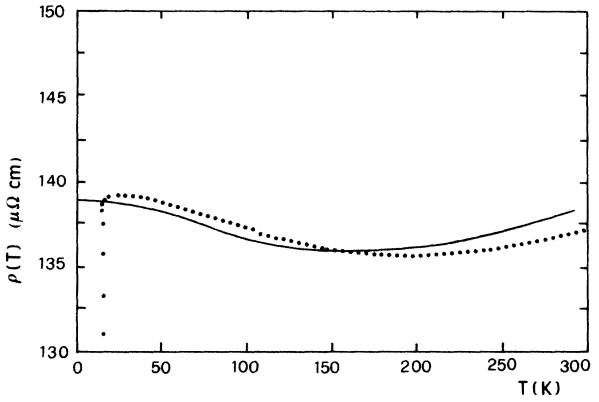

FIG. 3. Electrical resistivity ρ as a function of the temperature T for a sample with $r = 0.98$. The continuous line represents the theoretical prediction [Eq. (3); see text].

$[\rho_\infty(300\ \mathrm{K}) = 57\ \mu\Omega\,\mathrm{cm}]$ compares in any case fairly well with the values reported in the literature for bulk NbN.[1]

In Fig. 2 the average film grain size D (deduced by x-ray diffraction) is reported as a function of the residual resistivity ratio r. A relation between r and D can be again deduced by Eq. (3). We get

$$r = r_\infty \left[\exp\left[\frac{AK}{D\rho_\infty(20\ \mathrm{K})}\right]\right]^{1/r_\infty - 1}. \tag{5}$$

Equation (5) is plotted in Fig. 2 (continuous line) for $r_\infty = 2.2$, $\rho_\infty(20\ \mathrm{K}) = 26\ \mu\Omega\,\mathrm{cm}$ and $AK = 7\times10^{-5}\ \mu\Omega\,\mathrm{cm}^2 = \mathrm{const}$.

It is interesting to observe that for $r > 1$ we can fit the data using a fixed value for the parameter A while for $r < 1$ we cannot. This implies that for the high-quality films ($r > 1$) the increase of the residual resistivity ratio can be accounted for assuming only an increase of the average grain size D in the films. If we assume $K \cong (3-6)\times10^{-6}\ \mu\Omega\,\mathrm{cm}^2$ for NbN (as in most metals) we get $A \cong 10-20$ ($\Gamma \cong 10^{-5}-10^{-10}$) and hence a very poor coupling between the grains comes out even in the best cases.

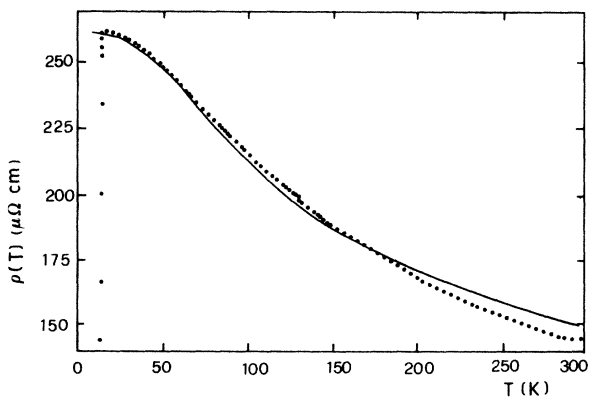

FIG. 4. Electrical resistivity ρ as a function of the temperature T for a sample with $r = 0.56$. The continuous line represents the theoretical prediction [Eq. (3); see text].

For the lower quality films ($r<1$) even larger A values have to be introduced to account for the results reported in Fig. 2 (for $r=0.50$ it is $D\cong 300$ Å, and from Eq. (5) we get $AK=22\times10^{-5}$ $\mu\Omega\,\mathrm{cm}^2$). In Figs. 3 and 4 the measured temperature dependence of the resistivity is reported for the samples exhibiting $r=0.98$ and 0.56, respectively.

The continuous lines represent the prediction from Eq. (3) where $\rho_\infty(T)$ was deduced by a measurement performed on a NbN film exhibiting a conventional metallic behavior ($r=1.6$). The constant AK was assumed to be temperature independent and was adjusted to obtain the best fit of the data. The agreement is very good in both cases over the whole temperature range.

The occurrence of a minimum in the resistivity in the range 100–150 K for samples with $r\cong 1$, already observed by several authors, is also well reproduced.

The temperature coefficient of resistivity,

$$\alpha(T)=[1/\rho(T)][d\rho(T)/dT]\ ,$$

can be also evaluated in the framework of the model by Hoffman and co-workers.

It is, in fact, from Eq. (3),

$$\alpha(T)=\alpha_\infty(T)\left[1-\ln\left[\frac{\rho(T)}{\rho_\infty(T)}\right]\right]\ , \tag{6}$$

where we have defined

$$\alpha_\infty(T)=\frac{1}{\rho_\infty(T)}\left[\frac{d\rho_\infty(T)}{dT}\right]\ .$$

The room-temperature TCR, $\alpha(300\ \mathrm{K})$, calculated by Eq. (6), assuming $\rho_\infty(300\ \mathrm{K})=57$ $\mu\Omega\,\mathrm{cm}$ and $\alpha_\infty(300\ \mathrm{K})=16\times10^{-4}\ K^{-1}$, is reported in Fig. 5 (continuous line).

This curve agrees faily well with the measured TCR (300 K) for all our samples.

The zero TCR corresponds to $\rho(300\ \mathrm{K})\cong 150$ $\mu\Omega\,\mathrm{cm}$. It is clear how the poor coupling between the grains in a polycrystalline sample can be very relevant in determining the α-ρ relation. In Fig. 5 the original Mooij plot for crystalline disordered metallic systems[8] (dashed area) and the more extended data collection recently reported by Tsuei[9] (dashed-dotted area) are also reported for comparison.

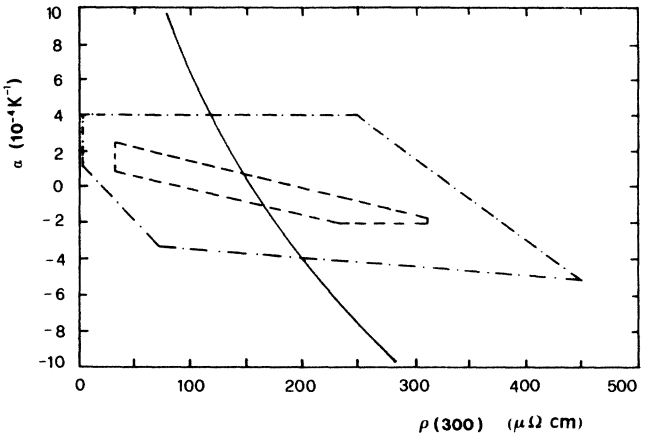

FIG. 5. Temperature coefficient of resistivity at room temperature, $\alpha(300\ \mathrm{K})$, as a function of the room-temperature resistivity $\rho(300\ \mathrm{K})$. The curve (continuous line) is obtained by Eq. (6), assuming $\rho_\infty(300\ \mathrm{K})=57$ $\mu\Omega\,\mathrm{cm}$ and $\alpha_\infty(300\ \mathrm{K})=16\times10^{-4}\ \mathrm{K}^{-1}$.

CONCLUSIONS

We have shown how the electrical resistivity of sputtered-deposited NbN films is strongly influenced by grain-boundary scattering.

Our results are very well described by a simple model introduced by Hoffman and co-workers.[5,6]

The analysis of the data in terms of this model gives a value $\rho(300\ \mathrm{K})=57$ $\mu\Omega$ cm for the intragrain (bulk) resistivity of our NbN films, and a maximum value $\Gamma\cong10^{-5}$ for the transmission probability through the grain boundaries.

"Nonmetallic" behavior and minima in the resistivity versus temperature dependences are also observed in our samples and naturally described in the framework of the same model assuming Γ to be temperature independent. The small value of Γ, and the fact that it is temperature independent lead us to the conclusion that tunneling is indeed the coupling mechanism between the grains in NbN. Finally, we point out that the presence of grain boundaries has a strong influence on the TCR versus resistivity (α-ρ) relation in polycrystalline samples.

ACKNOWLEDGMENTS

The authors are grateful to K. E. Gray for useful comments and suggestions and to B. Grozea, G. Perna, and F. Vicinanza for technical assistance.

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