Anomalous Resistivity of Nb_3Sn†

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The resistivity of several specimens of niobium stannide has been measured over the range 18–850°K. The resistivity rises rapidly up to 200°K and then approaches a linear variation with a considerably smaller slope. Over the entire range the resistivity can be fit to better than 1% by the form $\rho(T)=\rho_0+\rho_1T+\rho_2\exp(-T_0/T)$ where $\rho_0\approx1\times10^{-5}\Omega$-cm, $\rho_1=4.66\times10^{-8}\Omega$-cm/°K, $\rho_2=7.47\times10^{-5}\Omega$-cm, and $T_0=85$°K. Hall measurements made at 27, 77, and 300°K, if interpreted on a one-band model, indicate a constant hole density of 1.77×10^{22}/cc, and an effective valence of 0.27/atom. The anomalous resistivity can not be explained on the basis of present models of the resistivity of transition metals, although the constancy of the Hall constant implies that the scattering probability rather than the effective number of carriers is changing with temperature. The relevance of the present results to recent models of the electronic structure of Nb_3Sn is discussed.

THE resistivity of several specimens of niobium stannide has been measured over the range 18–850°K. The measurements were made on single-phase stoichiometric Nb_3Sn obtained by chemical reduction from the chlorides of Nb and Sn,[1] as well as on similarly prepared nonstoichiometric material ("Nb_4Sn") with the same β-tungsten crystal structure. Vapor deposited material presents several advantages for research on niobium stannide; perhaps the most important, is the fact that the material is single phase and of low impurity content ($\leq0.2\%$), and is thus considerably better defined than that prepared by the usual metallurgical techniques. For example, vapor deposited Nb_3Sn with a T_c of 18.3°K can have transition widths as low as 0.03°K, about a factor of 10 below any width reported in the literature for sintered or arc-melted material.

Apart from the high T_c of Nb_3Sn and other compounds with the β-tungsten structure, these materials have recently attracted interest due to the existence of pronounced temperature anomalies in such quantities as the Knight shift,[2] paramagnetic susceptibility[2] and the nuclear relaxation time[3] T_1. Although these anomalies were observed in β-tungsten compounds of the form V_3X, an analysis of the data[3] implies that the source of the anomalous behavior is more general, and arises from the peculiar chain structure of β-tungsten compounds.

The present experiments of Nb_3Sn add yet another anomalous temperature dependence, namely the electrical resistivity. The resistivity of all samples show marked departures from the usual temperature dependence of both transition and nontransition metals. Rather than the power-law-to-linear behavior characteristic of most metals, the resistivity rises rapidly up to about 200°K, and then saturates to a small linear dependence at the highest temperatures. A significant result of the present work is that the resistivity can be described by the following simple form to an accuracy of better than 1% over the entire temperature range 18–850°K.

$$\rho=\rho_0+\rho_1T+\rho_2\exp(-T_0/T), \quad (1)$$

where $T_0=85$°K and $\rho_2\approx5\rho_1\times(300°)$. While departures from the predictions of the simple theory of metals are to be expected for Nb_3Sn, the simple form of (1) is unexpected, and is difficult to interpret in terms of the usual modifications of the simple theory such as high mass narrow bands.

Table I lists the characteristics of some of the samples measured. All were prepared by vapor deposition on ceramic substrates, with the exception of FS 14 which was an unsupported film. Stoichiometry of the samples was determined by wet chemical analysis. X-ray and optical examination of anodized material indicate that the material is single phase. Electron microscope measurements indicate a crystallite size of the order of 2000 Å in diameter, which agrees well with the results of low-temperature thermal conductivity measurements[4] on similar material. The samples except for FS 14 were polished, and then cut to shape by sand blasting and had poorly defined areas. For this reason, FS 14 was used to obtain the absolute resistivity, and the other samples were normalized to it. This could be done quite successfully except for 65(6) which had a slightly different ratio of coefficients of the temperature-dependent terms, indicating the failure of Matthiessen's rule. For this sample one could determine the parameters in (1) in two ways: first using $T_0=85$°K, which gave a fit to about 10%, and then using $T_0=105$°K, which fits the data to better than 2% over the range T_c to 320°K.

Table I summarizes the resistivity coefficients obtained in this manner. Figure 1 shows the resistivity for FS 20 and 87 (1) from 18.3–850°K. As noted, the other

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[1] J. J. Hanak, in *Metallurgy of Advanced Electronic Materials*, edited by G. B. Brock (Interscience Publishers, Inc., New York, 1963), p. 161; G. W. Cullen (to be published).

[2] A. M. Clogston and V. Jaccarino, Phys. Rev. **121**, 1357 (1961). B. G. Silbernagel and M. Weger, Bull. Am. Phys. Soc. **7**, 614 (1962).

[3] M. Weger, Rev. Mod. Phys. **36**, 175 (1964).

[4] G. D. Cody and R. W. Cohen, Rev. Mod. Phys. **36**, 95 (1964).

TABLE I. Characteristics of specimens.

Specimen	wt% Nb[a]	T_c(°K)	ΔT_c(°K)	$\rho_0(10^{-5}\ \Omega\text{-cm})$	$\rho_1(10^{-8}\ \Omega\text{-cm/°K})$	$\rho_2(10^{-5}\ \Omega\text{-cm})$	T_0(°K)
FS 14	70.5±0.3	18.3	0.03	1.08	4.66	7.47	85
FS 20	70.5±0.3	18.3	0.04	1.08	4.66	7.47	85
81 (10)	71.2±0.3	18.2[b]	0.07	1.16	4.66	7.47	85
87 (1)	70.5±0.3	18.3	0.27	1.25	4.66	7.47	85
65 (6)	73.4±0.3	15.5	4.0	4.7	4.66	7.47	85
				4.7	6.92	7.68	105

[a] Nb_3Sn 70.1 wt.% Nb.
[b] Resistance determination, all others are by ac inductance.

stoichiometric samples show identical behavior except for small differences in residual resistivities. The smooth curve represents Eq. (1) with $\rho_0=1.08\times10^{-5}$ Ω-cm, $\rho_1=4.66\times10^{-8}$ Ω-cm/°K, $\rho_2=7.47\times10^{-5}$ Ω-cm, and $T_0=85$°K. In this figure we also show the exponential part of (1) compared to the difference between the measured resistivity and the first two terms of (1). One also notes in Table I the relative invariance of ρ_2 and T_0 for sample 65(6) for changes in the residual resistivity by almost a factor of 5. This result indicates that the failure of Matthiessen's rule is slight for large departures from stoichiometry, and that essentially the same mechanism governs the resistivity of stoichiometric and nonstoichiometric material. Indeed, previous data[5] on sintered Nb_3Sn can be interpreted in terms of (1) and gives essentially the same value of T_0, although the ratios of ρ_2 and ρ_1 differ by about a factor of 1.5 from the ratio derived from Table I.

As noted previously, there are several mechanisms that lead to departures from the temperature dependence predicted by the simple theory of metals. One considered by Mott[6] involves a high density of states at the Fermi level. The rapid variation of the density of states with energy leads to a contribution to all integrals involving the Fermi function of the form CT^2.

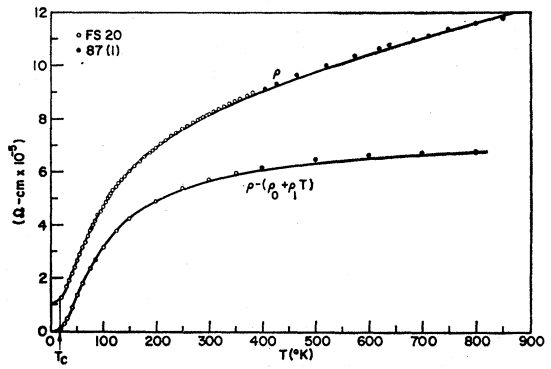

FIG. 1. Upper points, resistivity of Nb_3Sn as a function of absolute temperature. The curve shown is Eq. (1). Lower points the resistivity minus the residual resistivity and the linear term; the curve shown is the exponential part of Eq. (1).

In particular, if one considers the possibility of scattering into the high-density band from the low-mass band, there is an additional contribution to the resistivity which amounts to higher powers of T (up to T^3) in the temperature dependence. Wilson[7] has considered an elaboration of the Mott model where account is taken of the possibility that the high-density band is not at the same k vector as the conduction band. At high temperatures the resistivity is linear on T; at low temperatures there is an exponential drop off, reflecting the absence of high-temperature phonons.

There is some justification for applying either of these two models to Nb_3Sn. The high T_c of Nb_3Sn is suggestive of a high density of states at the Fermi level and the work of Clogston and Jaccarino[2] also implies a similar peak in the density of states. Unfortunately, calculations based on these models do not lead to the temperature dependence exhibited by the data. The resistivity can clearly not be represented by a simple power law even to terms of order T^3. Moreover, the Wilson calculation predicts a much smaller exponential contribution, relative to the linear term, than was observed. It is possible that there is a fortuitous compensation of terms arising from both the Wilson and Mott model.[8] The striking agreement of the simple form (1) with the data would appear to rule this out.

Two other mechanisms are more speculative. If one postulates the existence of localized states whose levels are split by the crystalline field one can, following Elliot,[9] obtain a contribution to the resistivity of the form

$$\rho\approx[\cosh(T_0/2T)]^{-2}, \qquad (2)$$

where k_BT_0 is the energy splitting. The present data can be fit to an accuracy of about 10% by (2) plus a linear term and the residual resistivity, with $T_0=147$°K. The departures from the data are too large, however, to place any confidence in this model, although it is in better agreement than those previously discussed. Another alternative is the one-dimensional model for Nb_3Sn introduced by Weger.[3] This model can lead to a relaxation time of the form

$$1/\tau\approx(\exp(T_0/T)-1)^{-1}, \qquad (3)$$

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[8] R. Smoluchowski, Phys. Rev. **125**, 1577 (1962).
[9] R. J. Elliott, Phys. Rev. **94**, 564 (1954).

where $T_0=(2S\hbar k_F/k_B)$, S is the velocity of sound, and k_F is the Fermi wave vector. If one used a velocity of sound of 3×10^5 cm/sec, T_0 from the data corresponds to $k_F\approx2\times10^7$ cm^{-1}. The free-electron model of Nb_3Sn, with the full valence of 4.75, would imply $k_F\approx2\times10^8$ cm^{-1}, while a one-dimensional lattice would imply $k_F\approx6\times10^7$ cm^{-1}, in fair agreement. Unfortunately, (3) would also imply a linear term too large compared to the exponential to fit the experimental resistivity.

Additional evidence for the source of the anomalous behavior of the resistivity of Nb_3Sn is provided by Hall measurements made at 27, 78, and 300°K in fields up to 7600 G. The Hall voltage was positive, independent of temperature, and in terms of a one-carrier model, implied a hole density of 1.77×10^{22} holes/cc. The effective valence of Nb_3Sn is thus 0.27 holes per atom, and the room temperature mobility is 4.3 cm^2/Vsec. Although quantitative interpretation of this Hall constant is difficult since it undoubtedly arises from multiple band effects, the temperature independence is significant for the present paper. Since, from 300–27°K, the resistivity changes by a factor of 6, the constant Hall voltage supports the view that the scattering time rather than the effective number of carriers is changing as the temperature is reduced, and would appear to rule out the Wilson-Mott model[8,10] for Nb_3Sn.

The present paper has shown the existence of a pronounced resistivity anomaly in Nb_3Sn, and demonstrated that the temperature variation can be fit to an accuracy of 1% from 18–850°K, by a surprisingly simple expression. Moreover, Hall measurements support the view that the anomaly arises from an unexpected rapid temperature dependence of the scattering probability, below 200°K. Unfortunately, a more quantitative treatment requires a better knowledge of the band structure and bonding in Nb_3Sn than is presently available, in particular, an analysis of the role played by the chains of strongly bonded niobium atoms. It is hoped that such a quantitative treatment of the structure of Nb_3Sn and its transport behavior may also lead to an understanding of the intriguing fact that this material has the highest T_c of any known superconductor (18.3°K).

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Study of Oscillations and Correlations in the Relaxation of a Model Spin System*

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A detailed investigation is made of the approach to equilibrium of system of spins with $I=1/2$. The spin-spin interaction $\Sigma_k \Sigma_{j<k} B_{jk}\sigma_x{}^j\sigma_x{}^k$ with B_{jk} constant is treated exactly, while the additional interaction $\Sigma_k \Sigma_{j<k} L_{jk}\sigma_x{}^j\sigma_x{}^k$ with L_{jk} depending on lattice vibrations is treated by means of the assumption of sufficiently short correlation times for the L_{jk} operators. All correlations between the L_{jk} are included. The effect of the correlations usually neglected is expressed in terms of a sum over states somewhat resembling an Ising-model partition function with the time replacing interaction strength. The oscillatory relaxation via the B_{jk} and the monotonic relaxation via the phonons compete with each other; interference effects between the two relaxation modes also occur; the origin and nature of the irreversibility are very different for the two relaxation modes.

1. INTRODUCTION

THE problem of nuclear magnetic relaxation via the dipole-dipole interaction in a crystal lattice is a many-body problem in which the correlations between spins at different sites play a role. At temperatures sufficiently low, so that the lattice is effectively rigid, the system of spins is an isolated system with a discrete system of energy levels; the approach to equilibrium of an initial polarization transverse to an applied static magnetic field is in this case oscillatory, as both the experiments and the explicit calculations of Lowe and Norberg have shown.[1] At high temperatures the dipole-dipole relaxation in solids is described by Bloch's general theory of relaxation,[2] in which the lattice vibrations play the role of a heat bath; the relaxation of an initial polarization transverse to the static magnetic field is in this case described by a sum of decaying exponentials. The occurrence of oscillations at low temperatures and their disappearance at high temperatures[3]

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