murti, and Chin.[8] Both these devices, however, offer elegant solutions only to a limited range of low-temperature experiments. On the other hand, a thin-film light-scattering spectrometer could, in principle, be applied to any solid and would not be restricted to low-temperature operation. Within its frequency range such a device could thus be a versatile complement to the inelastic-neutron-scattering spectrometers.

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Hopping Conduction through Localized States in Nb/Al_2O_3 Films*

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Electrical conduction in Nb/Al_2O_3 cermet films at low temperatures shows the presence of a new form of hopping conduction through localized states. In this mechanism the dielectric plays an essential role, behaving like an amorphous wide-band-gap semiconductor and acting as host to a distribution of localized states due to Nb dispersed, on an atomic scale, in the alumina matrix.

Electrical transport phenomena in thin films, obtained by co-deposition of a metal and a dielectric, have been extensively investigated of late because of their applications as resistive elements. These materials are also interesting from the point of view of electrical transport in disordered systems.[1-5]

Thin films of Nb/Al_2O_3 were obtained by co-evaporation from two independent sources onto fused-silica substrates. A detailed account of the preparation, structural investigation, and superconductivity of these films will be published elsewhere.[6]

Electron-microscope investigation showed the films to consist of quasispherical niobium particles imbedded in an Al_2O_3 matrix. In order to obtain different particle sizes, we varied the concentration of Nb as well as the temperature of deposition and annealing.

Films containing 85–95 wt% Nb, as known from the controlled evaporation parameters, were deposited on substrates maintained at 550°C and had a mean particle size $2r$ of about 32 Å. These films showed metallic-type conduction with a relatively small temperature coefficient of resistivity ($+6.6\times10^{-4}$ °K^{-1}), and became superconductive below 5.2°K.[6] Films containing 71 wt% Nb with $2r \simeq 20$ Å[7] (deposited at room temperature) had an activated conduction with activation energies ΔE increasing monotonically (Fig. 1, curve *a*) between 0.5×10^{-6} eV at 1.9°K and 4.4×10^{-3} eV at 300°K. This monotonic variation of

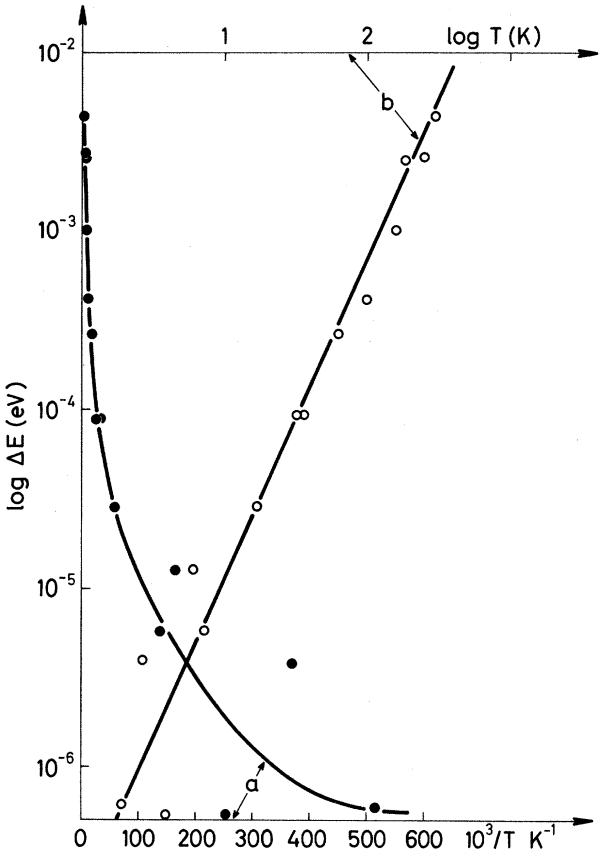

FIG. 1. Curve *a* (closed circles), dependence of the activation energy versus reciprocal temperature obtained from the $\ln R(1/T)$ curve. Curve *b* (open circles), activation energy versus $\ln T$ dependence

the activation energy with temperature over a large temperature range is indicative of the fact that we do not have a mixture of pure metallic and activated condution processes in these 71-wt%-Nb films.[8]

Electrical transport in granulated-metal films normally involves activated tunneling between metal particles separated by potential barriers.[9,10] The activation energy in this case is constant, as a function of temperature, and is due to electrostatic image forces. It can be considered as inducing a decrease of the Fermi level E_F' in the supply particle by δE_F, as shown in Fig. 2. In the low-field case

$$\delta E_F = \frac{e^2}{\epsilon\epsilon_0}\frac{r+s}{r(2r+s)},$$

where e is the electronic charge, ϵ and ϵ_0 are the respective permittivities of the matrix and of free space, r is the particle radius, and s is the mean separation between the edges of the

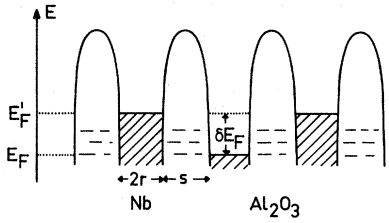

FIG. 2. Sketch of the electronic energy-level scheme in Nb/Al_2O_3 films.

particles. In our case, taking $\epsilon = 8.8$ for Al_2O_3,[11] $2r = 20$ Å and $s = 23$ Å, gives $\delta E_F = 0.13$ eV. As our highest experimental activation energy is more than 1 order of magnitude below this value, conduction cannot be by simple ionization of a metal particle and must be taking place on states much closer to the Fermi level. Such states are not available in the particles and, anyway, the 23-Å spacing between the edges of the particles would limit direct tunneling. Hence, the current that has been observed must be flowing through localized states in the matrix in which the particles are imbedded. These states are presumably due to Nb dispersed on an atomic scale.[12] The continuous variation of the activation energy with temperature points to these states having a continuous density distribution on the energy scale.[13] This is not unlikely as the presence of the metal will introduce local deformations into the alumina matrix structure, as well as acting as a dopant.

Consider a continuous distribution of localized states on the energy scale, with density of states $N(E)$ and carrier mobility $\mu(E)$.[13] The elemental conductance due to the carriers of energy E is then

$$\sigma_E = eN\mu \exp[-(E - E_F)/kT],$$

where E_F stands for the Fermi level.

At a particular value of the energy, such that $d\sigma_E/dE = 0$, this elemental conductance will be a maximum and the major part of the current will flow at that energy. The above condition is equivalent to

$$\partial(E - E_F)/\partial \ln(N\mu) = kT. \quad (1)$$

In a graphical form, Eq. (1) states that the dominant current will flow at the point on a plot of $\ln(N\mu)$ against energy at which a straight line, of gradient kT, is tangential.[14]

A continuously rising activation energy $E - E_F$ requires that the (density of states) $\times$ mobility product curve should show continuous positive

curvature with respect to the energy axis. A relationship that does show such curvature is

$$N\mu = N_F\mu_F \exp[A(E - E_F)^p], \quad (2)$$

where $N_F\mu_F$ stands for the product $N\mu$ at the Fermi level. Assuming that such a relationship might apply to this system, we obtain from Eq. (1) an activation energy corresponding to the dominant current, at a temperature T:

$$E - E_F = (ApkT)^{1/1-p}. \quad (3)$$

The conventional activation energy ΔE, calculated from the experimental resistance data, in the Fermi-Dirac range

$$\Delta E = k\,\partial \ln R/\partial(1/T) = E - E_F$$

should depend on T as in (3), if the assumption in (2) is valid. Further,

$$\ln\Delta E = \ln[(Apk)^{1/1-p}] + [1/(1-p)]\ln T.$$

Figure 1, curve b shows a plot of the data for the 71-wt%–Nb specimen where a relationship $\ln\Delta E$ proportional to $\ln T$ can be clearly seen with the constant of proportionality as 1.8. Apart from one point the fit of the data is remarkably good over 4 orders of magnitude of activation energy and 2 orders of magnitude of temperature. Analysis of the data in terms of other localized conduction characteristics, i.e., $T^{-1/n}$ ($n = 4$,[15] $n = 7$[16]) did not lead to any other process being as well defined as that shown in the diagram. We consider that this is clear evidence that conduction in the disordered Al_2O_3 matrix is a localized conduction process but that it is dominated by a distribution in the density×mobility product of the localized states. Previously all localized conduction processes have been considered as occurring in regions where the density of states was constant and the mobility dependent on the temperature. If we assume that here the density×mobility product is of the form given in Eq. (2), we have $p = 0.44$ and the constant $A = 4.71$ $(\mathrm{eV})^{-0.44}$. These values can be checked against the raw resistance data for

$$\rho = (eN\mu)^{-1}\exp[(E - E_F)/kT]$$
$$= (eN_F\mu_F)^{-1} \times \exp[-(Ap)^{1/1-p}(kT)^{p/1-p}(p^{-1} - 1)]. \quad (4)$$

A $\ln R$-versus-$1/T$ plot calculated on the basis of (4) with the parameters A and p given above yielded good agreement with the experimental data, as can be seen in Fig. 3, after applying a normalization factor calculated at $10^3/T = 550^\circ\mathrm{K}^{-1}$.

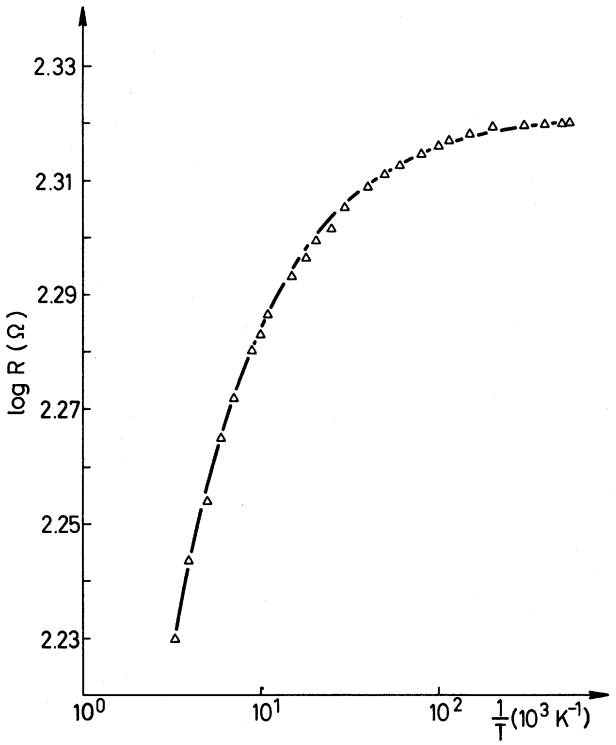

FIG. 3. Electrical resistance versus reciprocal temperature. Triangles, experimental values, averaged over four measurement series; solid line, calculated values using Eq. (4).

The product (density of localized states)×mobility is thus given by the law

$$N\mu = N_F\mu_F \exp[4.71(E - E_F)^{0.44}].$$

This law can be ascertained only up to 4.4×10^{-3} eV above the Fermi level (the limit of our experimental range of temperatures). Unfortunately it is impossible to differentiate between the density of states and the mobility in this expression, as only resistance has been measured. It is possible that high-field effects, where the current becomes nonlinear with applied field, would allow determination of these two factors independently.

We believe that the results on Nb/Al_2O_3 films with 71 wt% or less Nb in the temperature range below room temperature show the presence of a new form of localized conduction in which the dielectric plays an essential role and behaves like an amorphous wide-band-gap semiconductor which has been highly, and nonuniformly, doped by the niobium. If the doping had been uniform, or if localized intrinsic trap states of uniform density had been present, then the system would probably have exhibited Mott's $T^{-1/4}$ trapping law. As it is the system shows neither this character-

istic, nor the characteristic behavior of thermally assisted tunneling expected of a discontinuous metal film. The localized states in the oxide must be related to atoms or very small particles of Nb (below the resolving power of the electron microscope), which give rise to traplike localized levels extending in the forbidden gap of the Al_2O_3. Figure 2 shows the proposed scheme of electronic energy levels in the system Nb/Al_2O_3.

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Distortion-Enhanced Optical Absorption in $SrTiO_3$ at the Cubic-to-Tetragonal Transition

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We present thermomodulated optical absorption data near the fundamental edge of $SrTiO_3$ which gives, at the cubic-to-tetragonal phase transition, the first evidence of a second-order transition affecting the electronic energy levels. Enhanced absorption at the indirect gap energy is observed and attributed to relaxation of momentum conservation, via electron scattering at fluctuating domain boundaries. This extra absorption peaks at the transition temperature, where phase fluctuations are maximum.

Second-order phase transitions in crystals are the object of intensive investigation.[1] Structural changes are connected with phase instabilities, and they are discussed in terms of soft modes. This is the case of the cubic-to-tetragonal transition in $SrTiO_3$, which occurs at $T_0 \simeq 105$°K involving a rotation of neighboring TiO_6 octahedra in opposite directions around one of the cubic axes.[2] This transition, below which a deviation from the Curie-Weiss law[3] and from linear ther-