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The Meyer–Neldel rule in non-metallic YBa$_2$Cu$_3$O$_y$ films

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Abstract
We have observed the Meyer–Neldel rule and the inverted Meyer–Neldel rule for the first time in YBa$_2$Cu$_3$O$_y$ films. The data are explained in terms of the statistical shift of the Fermi level, by assuming a proper density of state in the charge-transfer gap.

In copper oxides, the metal–insulator (M–I) transition can be observed by removing oxygen atoms from the Cu–O planes (Aubin and Gagnon 1988). The cross-over from the metallic superconducting phase to an insulator occurs by shifting the Fermi energy through the mobility edge (Heeger and Yu 1993).

In the insulating state, the temperature dependence of the dc conductivity is found to obey the Arrhenius relation. An extrapolation of a set of Arrhenius plots with different slopes shows a well defined common intersection point at a finite temperature $T_{MN}$. If $T_{MN} > 0$, this is known as the compensation law or the Meyer–Neldel (MN) (1937) rule, and, in the case when $T_{MN} < 0$, this is called the inverted MN rule (Lucovsky and Overhof 1993). According to the MN rule, the dc conductivity is given by

$$\sigma(T) = \sigma_0 \exp\left( - \frac{\Delta E}{kT} \right),$$

(1)

with

$$\sigma_0 = \sigma_{00} \exp\left( \frac{\Delta E}{kT_{MN}} \right),$$

(2)

where $\sigma_{00}$ is a constant and $E_{MN} (= kT_{MN})$ is a slope parameter referred to as the MN energy. This relation has been applied to different types of semiconductor such as crystalline semiconductors (Narasimhan and Arora 1985), amorphous semiconductors (Irsinger et al. 1983, Overhof and Beyer 1983), organic semiconductors (Eley 1967, Kemeny and Rosenberg 1970), liquid semiconductors (Fortner et al. 1993), etc.

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1995), alkali-halide-type crystals and superionic conductors (Uvarov and Hairetdinov 1986), glasses (Shimakawa and Abdel-Wahab 1997), doped microcrystalline silicon (Lucovsky and Overhof 1993), and porous silicon (Lubianiker and Balberg 1997). In this letter, we report the first observation of the MN and the inverted MN rules in YBa$_2$Cu$_3$O$_y$ (YBCO) films.

Thin films of YBCO were prepared by the metal–organic chemical and vapour deposition technique and the details of preparation have been presented elsewhere (Higashiyama et al. 1991). The films were heat treated in an oxygen-reduced atmosphere for several hours, to reduce the oxygen content of the samples. The primary effect of removing oxygen is to reduce the hole concentration in the CuO$_2$ planes. Planar gap-cell electrodes using Ag were deposited onto the films.

The full and open circles in figure 1 show a semilog arithmetic plot of the pre-exponential factor against activation energy for 14 annealed samples of YBCO. The data given by the full circles ($\Delta E > 0.2$ eV) obey the MN rule with $E_{MN} = 48$ meV and $\sigma_{00} = 5 \times 10^{-3}$ S cm$^{-1}$, and the data given by the open circles ($\Delta E < 0.2$ eV) obey the inverted MN rule with $E_{MN} = -33$ meV and $\sigma_{00} = 6 \times 10^{2}$ S cm$^{-1}$.

Several models have been proposed to explain the MN rule (Kemeny and Rosenberg 1970, Roberts 1971, Overhof and Thomas 1989, Yelon et al. 1992).

Figure 1. The MN rule plot of $\sigma_0$ against $\Delta E$ for YBCO. (○), experimental data; (- - - - -) calculated result obtained by assuming a DOS given by figure 2, curve A; (-----), calculated result obtained by assuming a DOS given by figure 2, curve B.
One of these explanations is based on the statistical shift of the Fermi level (Overhof and Thomas 1989). This model has been applied successfully to hydrogenated amorphous silicon (a-Si:H), and also predicted the inverted MN rule at lower activation energies. Following Overhof and Thomas (1989), to calculate the Fermi level shift with temperature, the following charge conservation law should be satisfied:

$$\int N(E) f(E, E_F(T), T) \, dE = \text{constant}, \quad (3)$$

where $f$ is the Fermi-Dirac distribution function and $N(E)$ is the density of states (DOS) in the charge-transfer (CT) gap. The model of localized DOS used in this study is sketched in figure 2. To calculate the statistical shift for all samples, we assume only two representative Gaussian distributions of the localized DOS in the CT gap, which are shown in figure 2. The statistical shift of the Fermi level is not very sensitive to the shape and magnitude of DOS. The DOS given by curve A was used to calculate $E_F(T)$ for relatively high-oxygen-content samples. The Fermi level lies near the band edge in this case. For low-oxygen samples, the DOS given by curve

Figure 2. Assumed DOS used in this calculation given by $N(E) = N_1 \exp\left[\frac{-(E/a)^2}{2}\right] + N_2 \exp\left[-((0.7 - E)/b)^2\right]$, (· · · · · ·), curve A, DOS with $N_1 = 10^{22}$, $N_2 = 10^{18}$, $a = 0.13$ eV and $b = 0.23$ eV; ( ), curve B, DOS with $N_1 = 10^{21}$, $N_2 = 10^{15}$, $a = 0.11$ eV and $b = 0.45$ eV. The energy of the valence band is set to zero.
B was used for calculation and the Fermi level lies near midgap. In fact, these pictures of DOS are supported by optical measurements (Fujimori 1992).

Note that YBCO is thought to be p type owing to the existence of holes in the Cu 3d–O 2p band. If we consider the Fermi-level shift, the activation energy with respect to $E_V (= 0 \text{ eV})$ in equation (1) can be expressed as

$$
\Delta E = E_F (T) - E_V = E_F (0) + \gamma_F T,
$$

where $\gamma_F$ can be obtained numerically by differentiating equation (3) with respect to temperature. Let us assume, for example, that $E_F (0) = 0.3 \text{ eV}$ and the DOS represented by curve B. We then calculate the variation in $E_F (T)$ with temperature and the results are shown by the solid curve in figure 3. In a certain temperature range, the solid curve can be approximated by the following linear relationship:

$$
\Delta E = E_F (T) - E_V = E_F^* (0) + \gamma_F^* T,
$$

![Figure 3. Calculated Fermi $E_F (T)$ as a function of temperature: (---), approximate linear relationship between the Fermi energy and temperature.](image-url)
where \( \gamma^*_F \) and \( E^*_F(0) \) can be deduced from the slope of \( E_F(T) \) against \( T \) over a limited temperature range (broken line in figure 3) and from the extrapolation of \( E_F(T) \) at \( T = 0 \) K respectively. Combining equations (1) and (5), one obtains
\[
\sigma(T) = \sigma_0 \exp \left( \frac{\gamma^*_F}{k} \right) \exp \left( - \frac{E^*_F(0)}{kT} \right).
\]
(6)

The values of \( \gamma^*_F \) and \( E^*_F(0) \) can be calculated for each \( E_F(0) \). The broken line and solid curve in figure 1 are obtained in this way for the DOSs given by figure 2, curves A and B respectively. Here we used \( \sigma_0 = 400 \text{ S cm}^{-1} \) which is close to the minimum metallic conductivity (Mott and Davis 1979). The fit to the experimental data appears to be reasonable for the MN (\( \Delta E > 0.2 \text{ eV} \)) and the inverted MN (\( \Delta E < 0.2 \text{ eV} \)) regions.

Finally we discuss the origin of the Gaussian distribution of DOS in the band tail region. This kind of DOS may originate from potential fluctuations. The potential fluctuations in the present system can be introduced as follows. It is well known that in YBCO the density of charge carriers in the Cu–O planes correlates with the oxygen content. After annealing, some O atoms are removed from the Cu–O planes and hence the residual O atoms are distributed randomly through the films. This mesoscopic inhomogeneity owing to the random distribution of O may produce mesoscopic or macroscopic potential fluctuations in the valence- and conduction-band edges, as proposed for doped semiconductors (Shklovskii and Efros 1984) and for amorphous semiconductors (Overhof and Thomas 1989).

In summary, we have found the MN and the inverted MN relations in YBCO films. Assuming a Gaussian DOS in the charge-transfer gap, both the MN and the inverted MN effects are interpreted in terms of a statistical shift of the Fermi level. A random distribution of O through the Cu–O planes may be the origin of the Gaussian distribution of DOS in the CT gap.

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