The Hysteresis of Piezoconduction in Some Metallo-Organic Polymers

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Within recent years, the piezoconduction of many molecular organic solids has been studied. Usually, high-pressure compaction of polycrystalline samples is necessary, since large single crystals of most of these materials are not available. A thin compacted wafer of the molecular solid is formed from the polycrystalline sample by employing high-pressure techniques. After formation of the wafer, the resistance or conduction of the sample is studied as pressure is varied.

Certain materials exhibit anomalous behavior after being exposed to high pressures, in that their initial properties are not reproduced when the pressure is lowered. This behavior, termed hysteresis, may be due to such effects as: permanent change of phase, pressure-induced chemical modifications, and/or molecular orientation. This paper deals with the hysteresis of piezoconduction in two copper-complexed organic polymers.

The anomalous behavior of the piezoconduction of two copper coordination polymers, N,N'-dimethyldithiooxamido-Cu (II) (SK3A) and N,N'-dicyclohexyldithiooxamido-Cu(II) (SK1A) was initially reported by Hartman and Kanda (1965). Since that time, further investigation has been completed; the results are reported herein.

PREPARATION OF SAMPLES

Sample SK3A was precipitated by mixing one molar equivalent of purified N,N'-dimethyldithiooxamide in hot 50% ethanol-water solvent with one molar equivalent of copper sulfate in hot water. After centrifugal separation, the finely divided precipitate was subject to extraction in a Soxhlet apparatus with water and ethanol to remove both ionic and nonionic impurities.

N,N'-Dicyclohexyldithiooxamide in warm benzene solution was mixed with equimolar copper acetate in ethanol solution to produce SK1A. After centrifugal separation, the gelatinous precipitate was subjected to extraction with water and benzene in a Soxhlet apparatus.

Each of the samples is a fine-grained black insoluble powder. The structure is believed to be as shown in Figure 1 (Kanda, et al. 1967).

PIEZOCONDUCTION MEASUREMENTS

Piezoconduction measurements of the samples were made over a range of pressure and temperature from 0 to 14 Kbars and from 10 to 100 C. A Bridgman opposed-anvil high-pressure apparatus was used. The sample was contained in a pyrophyllite retaining ring (10 mm O.D. $\times$ 6 mm I.D. $\times$ 0.38 mm thick) and placed between the load-bearing surfaces of tool steel anvils. A Pasadena Hydraulic Model SB230C 50-ton press, with built-in thermostatically controlled platens, was used to produce the pressure and temperature regulation. The press was calibrated by standard strain gage measurements.

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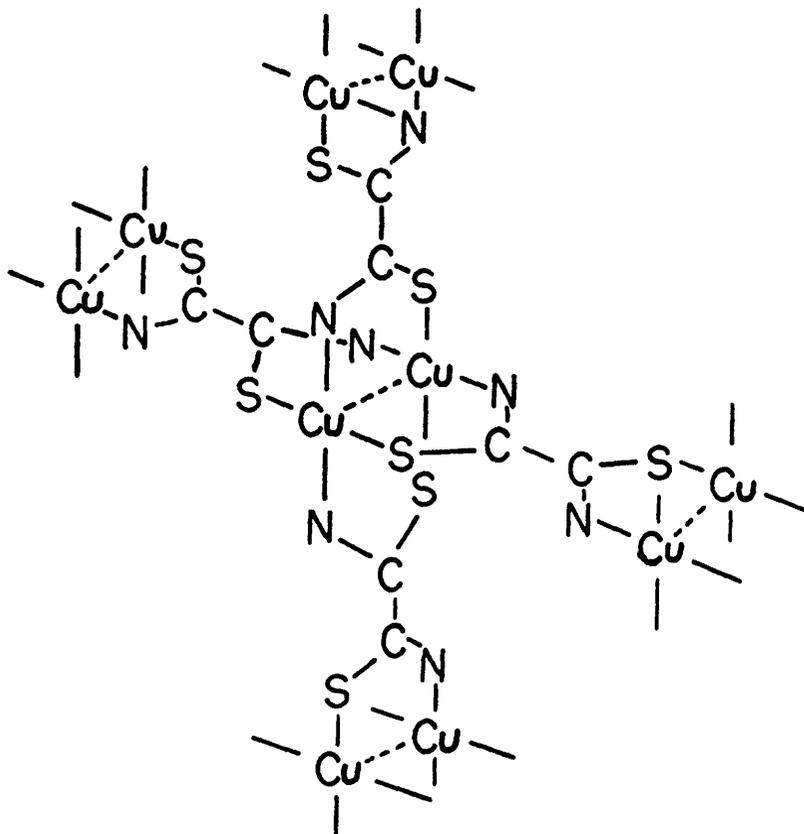
Figure 1. Molecular structure for *N,N'*-disubstituted-dithiooxamido-copper polymer. For simplicity, substituted radicals on nitrogen atoms are omitted.

Since many organic solids exhibit electric field dependence of the resistivity (Rosen and Pohl, 1966) it was necessary that the voltage across the sample be held constant during the experimentation. A Heathkit 1P-32 D.C. power supply, set to maintain a constant voltage of 5 volts, together with a Keithley 610B electrometer as an ammeter were used to accomplish this. The area and thickness of the sample were determined at the conclusion of each experiment, from which the resistivity could then be obtained.

By plotting resistivity (or conductivity) versus pressure for various temperatures, a family of curves is obtained (Pohl et al., 1962). Likewise, by plotting resistivity versus reciprocal temperature (at constant pressure), a second family of curves is obtained. The activation energy of conduction is computed from the latter curve.

As mentioned earlier, preliminary data on the polymers indicated the presence of mild hysteresis. Figure 2 shows a typical resistivity versus temperature curve for SK3A; curve (a) corresponds to the initial set of data with maximum temperature 75 C. The pressure was maintained con-
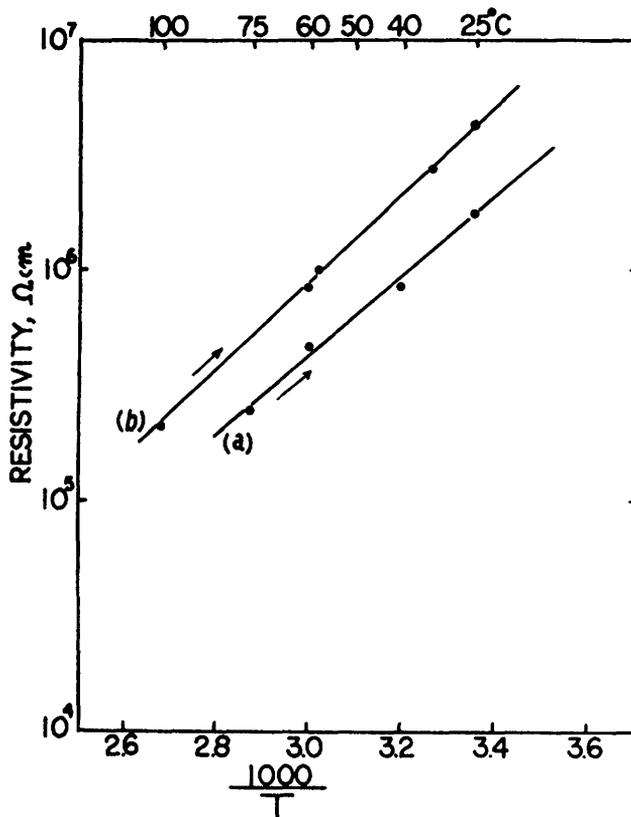
Figure 2. Resistivity vs. temperature for *N*,*N*'-dimethyldithiooxamido-
copper polymer (SK3A) at 14 Kbars. Curve (a) corresponds
to a maximum temperature of 75 C, while curve (b) corre-
sponds to a maximum temperature of 100 C.

stant at 14 Kbars. From curve (a) the activation energy is found to be
0.35 eV.

After cooling back to room temperature, the specimen was heated
to 100 C with curve (b) resulting. Since curves (a) and (b) differ only
slightly in slope, the activation energies appear to be nearly the same.
However the absolute values of resistivity have approximately doubled.
Typical resistivity-pressure curves for SK3A are shown in Figures 3 and
4. It can be seen that the pressure dependence is quite different for the
75 C maximum temperature sample and the 100 C one. Actual data on
SK1A is not presented here, but in general it behaves as does SK3A
(Hartman et al., 1967).

In view of the change in resistivity exhibited by curves (a) and (b)
in Figure 2, we decided to look at the behavior of the polymers over an
extended period of time. This resulted in a "quasi-closed" hysteresis loop
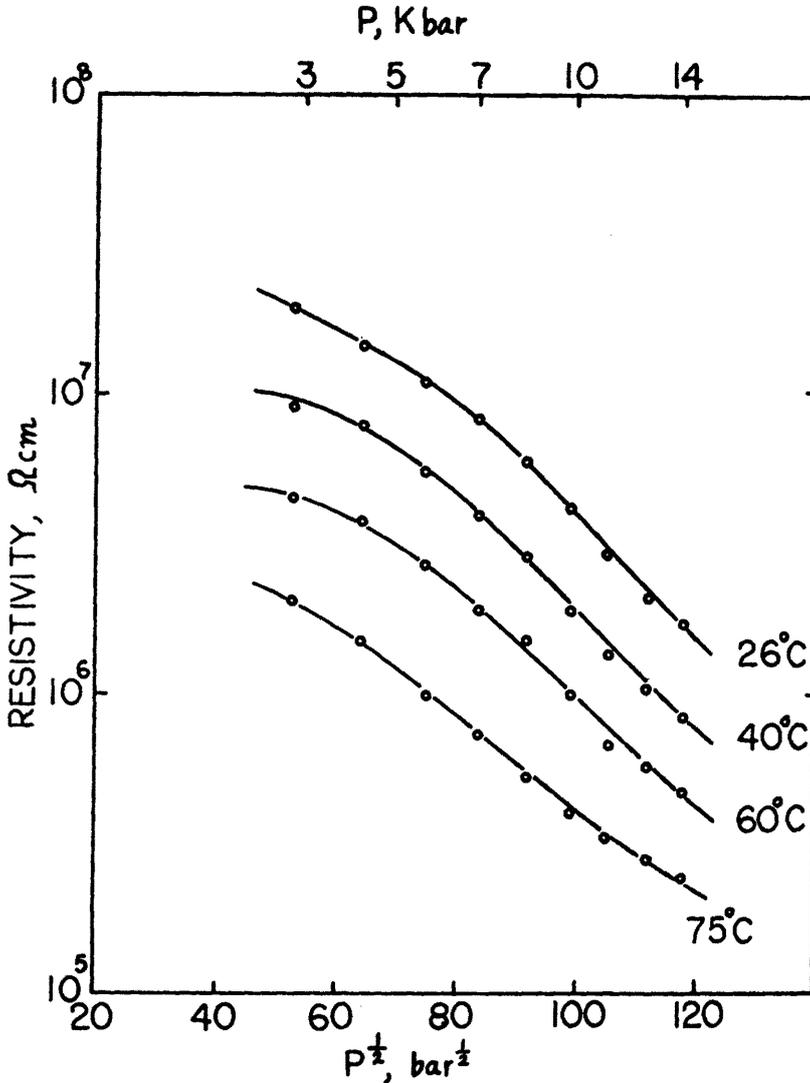being obtained.

Figure 3. Resistivity vs. pressure for SK3A, starting from 75 C.

A typical hysteresis curve for polymer SK3A is shown in Figure 5. This curve is an idealization of the data taken but no loss of generality has been introduced since the actual data portrayed the same type of behavior.

In obtaining a curve such as that shown in Figure 5, the resistance of the sample was first measured at room temperature (T_1) and a pressure of 14 Kbars. This value of resistivity is represented by ρ_1. The pressure
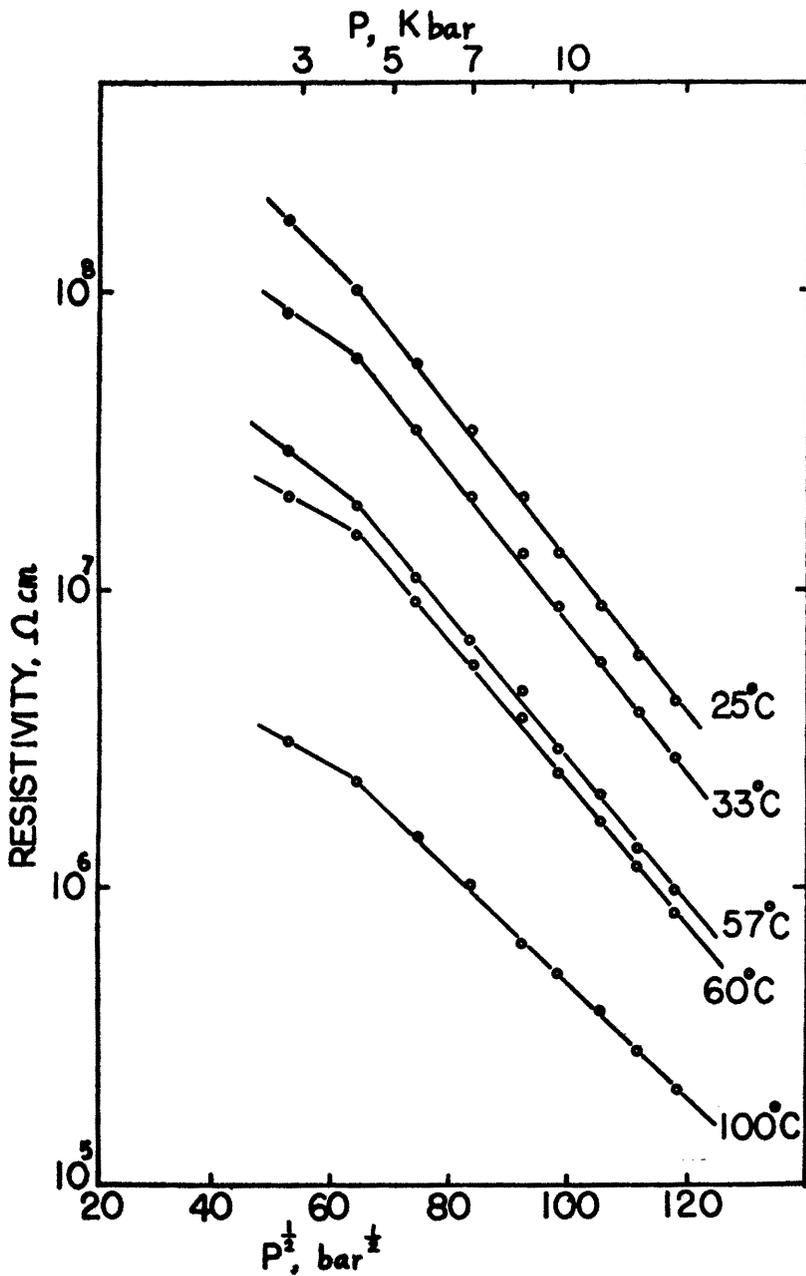
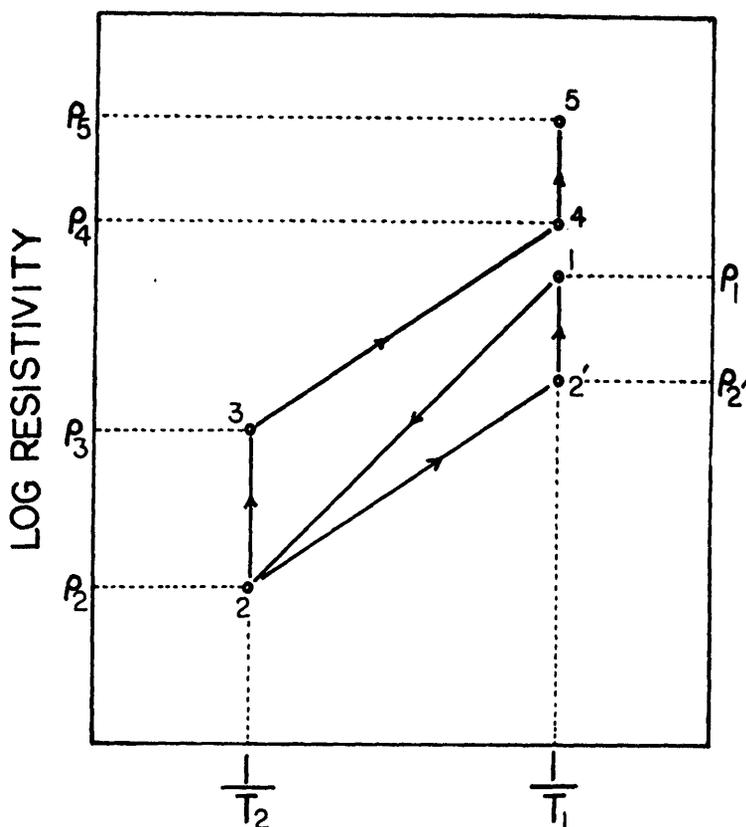Figure 4.   Resistivity vs. pressure for SK3A, starting from 100 C.

Figure 5. Idealized hysteresis curve for SK3A.

was then released and the sample was heated to higher temperature (T_1). Again the sample pressure was increased to 14 Kbars, and the resistance was measured (ρ_1). Two different procedures were then followed.

First, the pressure was held at 14 Kbars and the sample was quickly cooled back to room temperature, where the resistance was again measured (ρ_2'). The pressure was then released and the sample was allowed to relax. The resistance, which was periodically measured (always at 14 Kbars while the temperature was held constant), slowly increased back to its original value (ρ_1).

After returning to point (1), the sample was again heated to T_2, and point 2 was reproduced. This time, however, the sample was held at 14 Kbars and the resistance was periodically measured over a period of several hours. In this manner point (3) was obtained. Upon cooling to room temperature, the resistivity was measured at 14 Kbars as ρ_4.

In order to convert ρ_4 back to ρ_1, it was necessary to anneal the sample under 1 bar pressure for several hours. Otherwise, the resistivity tended to creep upward to a value ρ_5 as in the transition from ρ_2 to ρ_1.

In this manner, we were able to obtain a "quasi-closed" hysteresis loop for the resistivities of the copper-complexed polymers.

DISCUSSION OF RESULTS

In view of the complex behavior of the polymers, it appears that the conductivity, as measured, is some complicated function of pressure, temperature, and time.

We propose that the sample has two forms which can coexist, the forms being reversibly changed back and forth. These forms may represent different phases or different modes of bonding of the copper ions in the complexes.

On the basis of this "two form" solid, the net conductivity will also be dependent upon the concentration of each, since each form may have different conductivities.

Functionally expressing this dependence of conductivity upon the parameters, one obtains:

(1) $$\sigma = \sigma \ (T, \ P, \ t, \ f)$$

where T is temperature, P is pressure, t is time, and f represents the relative concentration of the form of the material present.

For a well behaved intrinsic semiconductor, the conductivity is given by:

(2) $$\sigma = |e| \ n\mu$$

where e is the electronic charge, n is the number of carriers per unit volume, and μ is the carrier mobility.

With reference to the proposed "two-form" solid, we must choose one of several available empirical expressions for the conductivity. The simplest one is perhaps that of direct additivity, i.e.,

(3) $$\sigma \cong \sigma_1 \ f_1 \ + \ \sigma_2 \ f_2$$

where:

(4a) $$\sigma_1 = |e| \ n_1 \ \mu_1$$

(4b) $$\sigma_2 = |e| \ n_2 \ \mu_2$$

Hence, σ may be written as:

(5) $$\sigma \cong |e| \ [n_1\mu_1 \ f_1 \ + \ n_2 \ \mu_2 \ f_2]$$

Now according to Eq. (1), Eq. (5) must show the proper dependence upon the variables $P, t,$ and T.

The normal temperature dependence is due to the carrier concentration dependence, which is given by

(6) $$n = n_0 \ \exp \ (-E/kT)$$

where E is the activation energy to produce a carrier pair, k is the Boltzmann constant, and T is temperature.

This dependence is of course observed; however, there may be another type of T dependence, perhaps through the rates of formation of forms f_1 and f_r.

The time dependence may now be introduced through the rates of formation of f_1 and f_r. At any instant of time, we assume that the rate of formation of f_1 is given by:

(7) $$(\partial f_1/\partial t)_{T,}P = k_t\ f_2 - k_b\ f_1$$

where k_t and k_b represent the forward and backward rate constants. The subscripts T and P indicate that temperature and pressure are being held constant, since the rate of formation is more than likely temperature- and pressure-dependent. Eq. (7) may be integrated to obtain a time dependence by recalling that the fractional concentrations must sum to 1, i.e.,

(8) $$f_1 + f_2 = 1$$

It should be noted however, that Eq. (7) is not rigorously true if the two forms of the solid involve different bondings. In that case, the linear dependence upon f_1 and f_2 must be replaced by a higher-order dependence.

The inclusion of the pressure dependence may be realized from a thermodynamic consideration of the activity coefficients of the two forms of the solid. This dependence appears to indicate an exponential pressure dependence upon the rate constants in Eq. (7).

In addition to the above mentioned pressure dependence, it is possible that the mobilities, μ, are also pressure-dependent. Pohl, et al. (1962) have seen such a dependence in several polyacene quinone radical polymers.

It can be seen, at least qualitatively, that the semiempirical formulation of the conductivity given by Eq. (3) will have the necessary dependence upon the variables involved.

This formulation presented here should not be considered as final. More consideration is being given to the pressure dependence. Additional data, including x-ray diffraction data, has been obtained, and it is planned to present this data, along with the completed theoretical model elsewhere (Hartman, Kanda, and Pohl, 1967).

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