

Activation nature of the relaxation of the electrical resistance in a quasi-one-dimensional compound Mo_2S_3

A. I. Romanenko, A. K. Dzhunusov, I. N. Kuropyatnitsk, and E. V. Kholopov
Institute of Inorganic Chemistry, Academy of Sciences of the USSR, Siberian Branch

(Submitted 17 January 1985)

Pis'ma Zh. Eksp. Teor. Fiz. **41**, No. 6, 237–239 (25 March 1985)

The relaxation times τ of the electrical resistance of Mo_2S_3 single crystals are measured over the temperature interval 0.98–145 K. Below 80 K, the relaxation times increase exponentially with decreasing temperature. The temperature dependence of the relaxation time can be explained in terms of the domain-wall-gas model, which is a typical model for the chains of the Mo atoms in the Mo_2S_3 structure.

Minute inorganic systems (NbSc_3 , TaS_3 , Mo_2S_3), in which metastable states have been detected—systems with a “memory”—have recently been a topic of considerable research interest.^{1–3} To determine the nature of the relaxation process in Mo_2S_3 single crystals, we have measured the temperature dependence of the relaxation time τ of the electrical resistance under conditions corresponding to a slight divergence from equilibrium.

The crystalline structure of Mo_2S_3 was studied by Deblieck *et al.*⁵ The Mo atoms in Mo_2S_3 form two types of crystallographically independent, zigzag chains with a metal-metal bond inside each chain. Deblieck *et al.*⁵ have shown that below 390 K each chain has a superstructure. Romanenko *et al.*³ have shown that below 180 K the compound Mo_2S_3 can easily be brought to a metastable state by means of rapid cooling.

The Mo_2S_3 single crystals used in our experiments were prepared by using the procedure described in Ref. 3. These single crystals had the dimensions $(5 \times 10^{-3}) \times 10^{-3} \times 5$ mm. A four-contact potentiometric method was used to measure the electrical resistance. The procedure for preparing the electrical contacts for measuring the electrical resistance within a relative accuracy of $10^{-4}\%$ is also described in

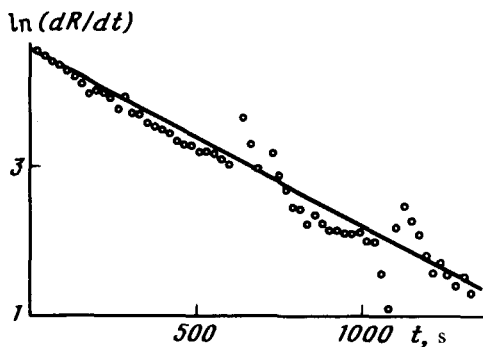


FIG. 1. Time evolution of the nonequilibrium electrical resistance (shown here is a typical time evolution; the measurements were taken at 76 K). The solid line represents the functional dependence $\ln(dR/dt) = A - t/\tau$, where A is a constant, and t is the time reckoned from the moment the temperature begins to change upon a transition to a new temperature at which the relaxation time τ is measured.

Ref. 3. A distinctive feature of the setup used for measuring the temperature dependence of τ was the installation of the thermometer and the heater directly on the sample holder. This procedure allowed us to cool the holder along with the sample and to stabilize them in less than 20 s at the temperature at which τ was measured and then to transmit every 20 s the experimental results of the measurements of the electrical resistance to a recorder over a time interval $(3-4)\tau$. Analysis of the experimental data was carried out by the method of least squares. Since we assumed that the time evolution of the nonequilibrium electrical resistance is exponential, we used the following expression to approximate the experimental results:

$$\ln(dR/dt) = A - t/\tau, \quad (1)$$

where R is the electrical resistance of the sample, A is a constant, t is the time reckoned from the moment the temperature begins to change upon a transition to a new temperature at which the value of τ is measured. Differentiation among the experimental data was performed according to the difference scheme. A typical curve (the measurements were taken at 76 K) is shown in Fig. 1. The measured values of τ were used to determine the temperature dependence of the relaxation time $\tau(T)$. Below 80 K, we see a sharp increase in τ as the temperature is reduced (τ increases by a factor of 40 as the temperature is reduced from 78 K to 71 K), in accordance with an exponential law

$$\tau(T) = \tau_0 \exp(\Delta/kT). \quad (2)$$

The confidence interval over which the parameters τ_0 and Δ/k in Eq. (2) change in terms of the Student coefficients at the 0.9 level with 6 points is estimated to be⁴

$$\tau_0 = (2.9_{-1}^{+3}) \times 10^{-13} \text{ s}, \quad \Delta/k = (2.7_{-0.9}^{+2.7}) \times 10^3 \text{ K}. \quad (3)$$

The first two values of τ had a large experimental spread at 78 and 77 K (Fig. 2), so that they were rejected in the evaluation for the functional dependence of the type in (2).

According to the data of Ref. 5, the period of the superstructure wave in Mo_2S_3 along each chain of Mo atoms includes 4 atoms which are displaced cyclically in four directions in the plane of the chain at a spatial separation of $\sim 0.16 \text{ \AA}$. Since at low temperatures the principal excitation which determines the thermodynamics of a one-

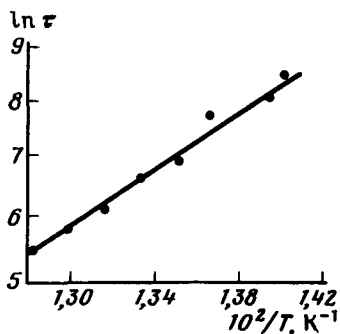


FIG. 2. Temperature dependence of the relaxation time of the electrical resistance τ . The solid line represents the functional dependence $\tau(T) = \tau_0 \exp(\Delta/kT)$, where $\tau_0 = (2.9 \pm 3) \times 10^{-13}$ s, $\Delta/k = (2.7 \pm 0.9) \times 10^3$ K.

dimensional system is the domain-wall gas,⁶ whose relaxation time increases in accordance with an exponential law as the temperature is reduced,⁷ we can assume that a corresponding relaxation time is applicable in other kinetic processes. We can thus determine the value of Δ/k in expression (2). Working from the aforementioned amplitude for the displacement of Mo atoms along the wave and assuming that the elastic modulus along the chain is typically $\sim 10^{12}$ dyn/cm², we estimate Δ/k to be $\sim 2 \times 10^3$ K. An analogous estimate of τ_0 as a typical phonon frequency along a chain yields a value of $\sim 3 \times 10^{-13}$ s. An agreement between these estimates and the results (3) obtained experimentally suggests that the relaxation processes observed by us are ionic in nature. On the other hand, the appearance of structural relaxation processes directly in the electrical resistance of Mo₂S₃ suggests that the conduction bands along the chains of the Mo atoms change significantly due to the appearance of superstructure. It would be logical to assume in this case that the resulting distortions are of a Peierls nature. In these distortions, the coherent displacement of the lattice sites is accompanied by the formation of a conduction-electron gap on the Fermi surface.⁸ Lending support to this assumption is a sharp change in the electrical resistance at temperatures at which the superstructures form along the chains of the Mo atoms.^{3,5} The presence of domain walls as centers of incoherent random scattering of an electron accounts for the finite electron density within the gap, which causes a reduction of the electrical resistance.

In summary, exponential retardation of the relaxation of the electrical resistance observed experimentally in Mo₂S₃ single crystals can be explained in terms of the model for the domain-wall gas in the one-dimensional chains of Mo atoms which are the composite part of the Mo₂S₃ structure.

¹R. M. Fleming, *Solid State Comm.* **43**, 167 (1982).

²G. Mihaly and L. Mihaly, *Phys. Rev. Lett.* **52**, 149 (1984).

³A. I. Romanenko, F. S. Rakhmenkulov, I. N. Kuropyatnik, V. E. Fedorov, and A. V. Mishchenko, *Phys. Stat. Sol. (a)* **84**, K165 (1984).

⁴L. Z. Rumshanskii, *Matematicheskaya obrabotka rezultatov eksperimenta (Mathematical Analysis of Experimental Results)*, Nauka, Moscow, 1971.

⁵R. Deblieck *et al.*, *Phys. Stat. Sol. (a)* **77**, 249 (1983).

⁶J. A. Krumhansl and J. R. Schrieffer, *Phys. Rev. B* **11**, 3535 (1975).

⁷E. V. Kholopov, in: *All-Union Symposium on Nonuniform Electronic States*, Novosibirsk, 1984, p. 100.

⁸R. E. Peierls, *Quantum Theory of Solids*, Clarendon Press, Oxford, 1955 (Russ. transl. IIL, Moscow, 1956).

Translated by S. J. Amoretty