Small polarons and the electronic properties of Mo_2S_3

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We investigate the small-polaron mechanism as a possible explanation of electrical-conduction and electrical-noise properties of the linear chain material Mo_2S_3. Experimental conductivity and noise data obtained in earlier papers [Phys. Rev. B **38**, 3973 (1988); Phys. Rev. B **39**, 5139 (1989)] are analyzed in terms of a small-polaron mechanism and a double-well potential model. We interpret the observed electronic properties in terms of kinetic equations describing the interaction of free carriers with fluctuations of density of the lattice. Appropriate kinetics equations to describe this interaction, which leads to small-polaron formation, are derived. These equations are found to explain quantitatively both the nonequilibrium electronic properties and electrical noise in Mo_2S_3.

I. INTRODUCTION

Mo_2S_3 is a conducting linear chain compound that undergoes phase transitions below room temperature to incommensurately distorted structures.[1–3] First-order phase transitions at 182 and 145 K show considerable hysteresis, and resistivity measurements show that these transitions involve a loss of Fermi surface.[4–8] In two previous papers, Fagerquist, Kirby, and Pearlstein carried out resistivity, thermopower, nonequilibrium pulsed conductivity, and electrical-noise measurements of Mo_2S_3 at temperatures below the phase transitions.[9,10] They were able to interpret their results at temperatures below the 145-K phase transition in terms of a phenomenological model in which the carries could exist in either a weakly conducting ground state or in a relatively highly conducting metastable state. Their results suggested that the behavior of the carriers could be well described by a double-well potential model, a schematic representation of which is shown in Fig. 1.

Figure 1 indicates the potential energy $U(q)$ of the charge carrier as a function of a configuration coordinate q. Possible physical interpretation of q will be discussed below. The well on the right-hand side of Fig. 1 corresponds to a weakly conducting ground state, while the well on the left-hand side corresponds to a relatively highly conducting metastable state. Fagerquist, Kirby, and Pearlstein[10] found the energy barrier W between the two states to be 0.254 eV and estimated the energy difference E between wells to be 10–20 meV. They also discussed three possible physical interpretations of the double-well potential, which we now summarize.

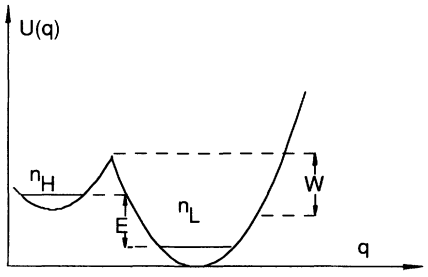

FIG. 1. Double-well potential model for carriers in Mo_2S_3. q-configuration coordinate. The carriers could be either in a low-conductivity ground state (right-hand side) or in a relatively high-conductivity metastable state (left-hand side).

A. The carrier trapping model

In this simple physical model, the carriers are trapped at impurity or other defect sites. To be consistent with experimental results, the defects would obviously have to produce a trapping site (potential-energy minimum) separated from the free-carrier state by a rather large potential barrier. In this case, the double-well potential would be a potential in real space, with the configuration coordinate q being a spatial coordinate. This model was ruled out for two reasons. First, no specific defects or impurities could be identified which could be responsible for the double-well potential. Second, while this model could produce the correct frequency dependence of the electrical-noise power observed by Fagerquist, Kirby, and Pearlstein, the calculated magnitude of the noise power was three orders of magnitude too small. The electrical noise in this model arises from random fluctuations of charge carriers between the two wells of the double-well potential. For this model to produce the correct magnitude of the noise, either the carriers would have to have a mobility of 4×10^4 cm^2/Vs (a very large value for transition-metal compounds), or 1000 carriers would have to cooperatively move from one well to the other.

B. The carrier-density wave model

In view of its linear-chain structure and presence of phase transitions to incommensurate distorted states, it

seems possible that Mo_2S_3 is a charge-density system similar to $NbSe_3$ or TaS_3.[11–13] Conduction in a charge-density wave system may involve cooperative motion of a large number of carriers. However, the properties of Mo_2S_3 are quite different from those observed in $NbSe_3$ or TaS_3. Mo_2S_3 does not show nonlinear conductivity at experimentally accessible electric fields. In NbS_3 for example, nonlinear conductivity is observed for applied electric field above a critical electric field. This additional conductivity is associated with coherent motion of large segments of the charge-density wave which have been depinned. Electrical noise associated with the depinning process is also observed in $NbSe_3$ for applied fields above the critical field.

In Mo_2S_3 electrical noise is observed for all applied fields; there is no critical field for the onset of the noise. The difference suggests that if Mo_2S_3 is a charge-density wave system, it must be quite different in character from $NbSe_3$ and TaS_3. Fagerquist, Kirby, and Pearlstein suggested a physical picture in which the charge-density wave was pinned by solitonlike kinks and antikinks. The destruction of kinks by thermal fluctuations would allow the segment to conduct. In that case, the double-well potential would be associated with kinds and antikinks, rather than with the individual free carriers. If the charge-density wave segment contained ~ 1000 carriers, this picture could explain the magnitude of the electrical noise. While this type of model is a promising candidate for explaining the electronic properties of Mo_2S_3 in qualitative level, existing theories of charge-density wave formation are not well-enough developed to derive estimates of the values of W and E or justify the carrier-density wave model.

C. The acoustic polaron model

Fagerquist, Kirby, and Pearlstein also considered that the double-well potential could arise from an acoustic polaron model. In this theoretically well-investigated model, an electron (or hole) can interact with a deformable lattice, and through this interaction the charge carrier can become localized in the lattice or "self-trapped."[14–17] It is important to stress, that along with the acoustic polaron ground state, a metastable state is also produced in which the charge carrier is untrapped, with an adiabatic potential barrier separating the trapped and delocalized states.

It was mentioned[9] that the small-polaron model does have two important points in its favor. First, it can give rise to a double-well potential of the type needed to explain the experimental results, if calculated values of W and E are happened to be similar to those experimentally determined. Second, the acoustic polaron model holds promise in its ability to explain the presence of the phase transitions. However, Fagerquist, Kirby, and Pearlstein pointed out that this model is essentially a single-carrier model and it could not explain the magnitude of the electric noise if we accept the simple mechanism of the noise due to fluctuations of number of carriers in double-well potential.[10]

Nevertheless, the present paper proposes the acoustic polaron model in more detail, taking into account both the real adiabatic potential and the kinetics of small-polaron formation in Mo_2S_3. We will see that the kinetics of small-polaron formation lead to a much larger electrical-noise amplitude comparable with experimental data.

Our model has the advantage of lack of adjustable parameters and it is based on adiabatic potential derived from experimentally justified values of the Fermi energy E_F and the effective carrier mass m^*.[5,18] Then the acoustic polaron model developed here can explain quantitatively both the nonequilibrium electronic properties and electrical noise in Mo_2S_3 at 100 K. We will discuss in detail the problem of existence of small polarons in Mo_2S_3 (small-polaron formation), approach to equilibrium of ensemble of carriers, and the noise power spectra. In contrast with Ref. 10, a large magnitude of electrical noise is explained in our model as a result of fluctuations of the number of fluctuations of density of lattice, rather than in terms of fluctuations of number of carriers in "frozen" double-well potential,[10] which gives the amplitude of electric noise three orders of magnitude less than in experiment.

II. SMALL-POLARON FORMATION

The main assumption in this paper is that small polarons are responsible for the unique electronic properties of Mo_2S_3, and we will propose appropriate kinetic equations to describe the formation and decay of self-trapped carriers. In particular, we will discuss the time- and temperature-dependent fluctuations in the local lattice density which are ultimately responsible for small-polaron formation.[14]

First let us discuss the possibility of the existence of small polarons in Mo_2S_3 on the basis of the general theoretical approach of Mott and Stoneham,[19] Sumi and Toyozawa,[15] and Toyozawa.[14] There is a hint that small polarons might exist in materials like Mo_2S_3 given by Mott.[20] The experiments[7,18] indicate that Mo_2S_3 has a narrow energy gap $E_G \approx 0.1$ eV and low Fermi energy $E_F \sim E_G$. According to Mott[20] in such materials electrons in narrow conduction bands are probably small polarons with enhanced mass $m^* \sim 10m_e$. The experimental value[5] $m^* \approx 7m_e$ is near to this value and that fact is a strong argument for existence of small polarons in Mo_2S_3. Nevertheless, we made an additional estimate below to check threshold requirements for polarons. It may be pointed out here that there are two kinds of coupling between electrons and phonons, which are responsible for two kinds of polarons, respectively:

(1) Frohlich interaction of electrons with optical phonons which may result in dielectric polaron.[16]

(2) Interaction of electrons with acoustic phonons, which may allow small-polaron formation. According to Deblieck,[3] Mo_2S_3 is a metallike material with metal-metal bonding between Mo atoms in quasi-one-dimensional chains and for that reason it seems unlikely that dielectric polarons can exist in this compound. Apart from that, the adiabatic potential $U(\Delta)$ (Δ is a dilation of lat-

tice for polarons) as was shown by Toyozawa,[14] has no potential barrier W between a ground polaron state and metastable conducting state. But this is in contradiction with experiments,[9,10] which indicate that nonzero value $W=0.25$ eV is principally important parameter to explain the electrical properties of Mo_2S_3 in the framework of double-well potential model. In other words, dielectric polarons (even if they exist in Mo_2S_3) are unlikely to be responsible for electric properties and for that reason they are not of our interest. The only difference between large acoustic and small acoustic polarons are their sizes and energies, but large polarons with size $l>R$ (R is atomic parameter) have a tendency to shrink to small polarons with $l\cong R$.[16]

In spite of the fact that small polarons are very promising candidates to explain electric properties of Mo_2S_3, there are two important threshold requirements for them to exist.[14] We shall discuss these requirements in detail and estimate the thresholds for their existence to demonstrate that small polarons can be found in Mo_2S_3.

The first necessary threshold requirement was formulated by Toyozawa[14] for a three-dimensional model. He considered interaction of carriers with acoustic mode using the concept of adiabatic potential $U(\Delta)$, which is due to the spherical volume dilation of radius R.

The dilation is assumed to be constant inside the sphere and zero outside it:

$$\Delta(r)=\Delta \quad (r<R)\,, \tag{1}$$

$$\Delta(r)=0 \quad (r>R)\,. \tag{2}$$

This dilation is considered as nothing but a three-dimensional square-well potential for the electron, which has a bound state if the depth of the well is sufficiently large, that is

$$\frac{-2m^*R^2E_1\Delta}{\hbar^2}\geq\left[\frac{\pi}{2}\right]^2. \tag{3}$$

E_1 and m^* are the deformation potential and the effective carrier mass, respectively. This threshold requirement allows us to calculate the critical dilation $\Delta=\Delta_{cr}$ which has the sense of a minimum dilation for a small polaron to form. If the critical dilation calculated from (3) happens to be greater than a typical fracture limit: $\Delta_{cr}>\Delta_{fr}\sim 0.2$–$0.4$, it should mean that small polarons cannot exist. Otherwise, if the critical dilation $\Delta_{cr}\leq\Delta_{fr}$, one can conclude that there is a bound state for the carrier and the material meets the first requirement (which is not enough for existence of small polarons).

The second requirement of Mott and Stoneham insists that this bound state is a real small polaron and self-trapping occurs only if its adiabatic energy is negative: $U(\Delta\geq\Delta_{cr})<0$. This is an important necessary threshold requirement and we should check both of them to be sure of the existence of small polarons in Mo_2S_3. To estimate the thresholds requirements, we used the following parameters taken from experiments:[5,18] $E_1\approx 2E_F/3\sim 0.06$ eV, $m^*=7m_e$, where m_e is the mass of electron and $E_F\approx 0.1$ eV is the Fermi energy in Mo_2S_3 measured from the band edge. The estimation based on the Eq. (3) gives a reasonable critical dilation $\Delta_{cr}=0.13<\Delta_{fr}$ (material meets the first requirement). It should be noted that Δ_{cr} might be even smaller because of the effect of dimensionality of electron subsystem in Mo_2S_3. It was shown that the bounding condition of Toyozawa is valid only for the three-dimensional problem. In contrast with the three-dimensional problem, the bounding is always possible for the one-dimensional model, as was shown by Holstein,[17] and there is no barrier W between stable (polaron) and metastable (free-carrier) state. Unfortunately, the effective dimensionality (d) of Mo_2S_3 is not known with any certainty and it seems that the electron subsystem is, rigorously speaking, neither one ($d=1$) nor three dimensional ($d=3$). Indeed, some authors suggest quasi-one-dimensional approximation to describe Mo_2S_3.[7–9] In Ref. 21 the temperature dependence of the anomalous part of the magnetic susceptibility χ_a was used to elucidate the problem of dimensionality in Mo_2S_3. It was shown experimentally that at 12 K the coherent length for the electrons $L_{int}=\sqrt{\hbar D_1/k_bT}$ (D_1 is the diffusion coefficient of the conducting electrons) is compared to the transverse dimensions of the quasi-one-dimensional filament. The authors concluded for that reason, that the quasi-one-dimensional approximation breaks down above $T=12$ K. The temperature of our experiment is $T=100$ K and one might think that the behavior of the electron subsystem is something between behaviors for one- and three-dimensional model. In other words, there is a serious reason to think that the real bounding condition is softer than (2) and $\Delta_{cr}\leq 0.13$. Let us check the second threshold requirement which, in fact, means the strong-coupling energy of a small polaron: $U(\Delta\geq\Delta_{cr})<0$.

In an attempt to design the adiabatic potential $U(\Delta)$ we shall follow the approach of Toyozawa[14] who suggested that

$$U(\Delta)=\frac{1}{2}C\frac{4\pi}{3}R^3\Delta^2-E_1(\Delta-\Delta_{cr}) \quad \text{for } \Delta\geq\Delta_{cr}\,, \tag{4}$$

$$U(\Delta)=\frac{1}{2}C\frac{4\pi}{3}R^3\Delta^2 \quad \text{for } \Delta<\Delta_{cr}\,. \tag{5}$$

Obviously, this potential is valid only for a small dilation $\Delta\ll 0.1$ when elastic energy represented by first terms in the right parts of (4) and (5) can be expressed by Hook's law. This approximation is not true for Mo_2S_3, where $\Delta>\Delta_{cr}=0.1$ and we must substitute the whole elastic potential $U_{el}(\Delta)$ into the expression for the adiabatic potential:

$$U(\Delta)=U_{el}(\Delta)-E_1(\Delta-\Delta_{Cr})$$
$$-\beta(\Delta_{cr}-\Delta)^2 \quad \text{for } \Delta_{fr}>\Delta\geq\Delta_{cr}\,, \tag{6}$$

$$U(\Delta)=U_{el}(\Delta) \quad \text{for } 0<\Delta<\Delta_{cr}\,, \tag{7}$$

$$U(\Delta)=U_{el}(\Delta)-E_F \quad \text{for } \Delta>\Delta_{fr}\,. \tag{8}$$

The last term in the right part of (6) reflects that the electron associated with the polaron suffers energy near to the Fermi energy E_F for $\Delta\leq\Delta_{fr}$. In this scheme, from analogy with linear polymers, we used the Morse potential to model the elastic part $U_{el}(\Delta)$ of the adiabatic potential:

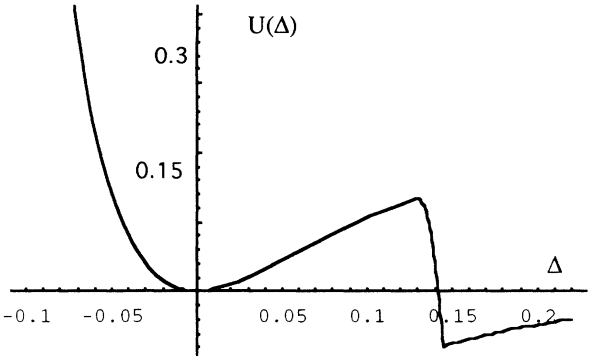

FIG. 2. Adiabatic potential for polarons. Deformation potential $E_1=0.1$ eV, critical deformation $\Delta_{cr}=0.13$, effective barrier $W=0.134$ eV, depth of the wall $E=-0.1$ eV, $T=100$ K. Potential $U(\Delta)$ is given in eV, Δ is dimensionless deformation of Mo-Mo bond.

$$U_{el}(\Delta)=D-2D\ \mathrm{Exp}[-\gamma\Delta]+D\ \mathrm{Exp}[-2\gamma\Delta]\ , \quad (9)$$

where parameters $D=0.14$ eV and $\gamma=12.1$ were calculated to correspond to the experimental elastic modulus[8] $C=2\times10^{12}$ dyn/cm^2 and the barrier of the double-well potential W.[9,10] The appropriate adiabatic potential calculated from (6)–(9) is shown in Fig. 2 and one can see that the requirement $U(\Delta>\Delta_{cr})<0$ is satisfied for $\Delta>0.145$. Moreover, the adiabatic potential $U(\Delta)$ has an effective barrier $W=0.13$ eV, that is not far from experimental data.[9] In conclusion, our estimate shows that Mo_2S_3 meets the small-polaron threshold requirements of Toyozawa, Mott and Stoneham, Sumi, and Toyozawa[15] (which are just a consequence of the requirements of Refs. 14 and 19).

In other words, it seems that small polarons can exist in Mo_2S_3 and we will study how they affect electronic properties, including electrical noise. In the next section, we consider this problem in more detail. In particular, we develop a set of kinetics equations which are then used to describe the nonequilibrium conductivity and electrical-noise behavior of Mo_2S_3.

III. KINETICS EQUATIONS

A. The thermodynamics ensembles

To begin, we assume that the double-well potential of Fagerquist, Kirby, and Pearlstein[9,10] originates from small-polaron formation as described above, and that the total density of carriers n_0 is constant. We can then write $n_0=n_L+n_H$, with $n_0\approx10^{20}$ cm^{-3}, where n_L and n_H are the carrier concentrations in the self-trapped (low conductivity) and free (high-conductivity) states, respectively. We further assume that penetration of the adiabatic potential barrier is thermally activated, and that its kinetics can be described by means of an effective kinetics constant K^+, which is a measure of the rate at which the carriers interact with lattice deformations. We also assume that the sample is homogeneous and that the thermally induced lattice deformations can be found anywhere in the crystal with the same probability. Then, the total density of states where deformations can exist is $n_d\approx R^{-3}$. The density of lattice fluctuations n_{Fl} with $\Delta=\Delta_{cr}$ (for small polarons to form) is of course expected to be much smaller than n_d.

In what follows, we consider only deformations with dilation $\Delta=\Delta_{cr}$. Obviously, fluctuations with $\Delta<\Delta_{cr}$ are not of interest as polarons cannot form. Similarly, fluctuations with $\Delta>\Delta_{cr}$ are not important because of the large thermal activation energy involved in forming them.

To begin, we will derive the kinetics equations for the densities of carriers in the high and low conductivity states (n_H and n_L, respectively) and for the density of fluctuations of lattice deformations of sufficient size to form a small polaron (n_{Fl}). To summarize, three ensembles are used in our model:

(1) The ensemble of carriers in the high-conductivity metastable state with mean density n_H.

(2) The ensemble of quasistable small polarons with mean density $n_L=n_0-n_H$.

(3) The ensemble of unstable (short-lived) deformations of the lattice of sufficient size ($l\sim R$) and dilation ($\Delta=\Delta_{cr}$) to trap a carrier. These deformations either disappear with a relaxation time $\tau_d\sim10^{-12}$ s, or they become small polarons after interaction with carrier. The mean density of these deformations was denoted above as n_{Fl}.

In order to write down the kinetics equations, we assume that the only interaction between these ensembles is the interaction of carriers in their high-conductivity (metastable) state with the lattice deformations, and this interaction is described by the single kinetics constant K^+. In accordance with both the general kinetics approach[22] and the double-well potential model, the kinetics equations for the various rates of change of density are expected to be

$$\frac{dn_H}{dt}=\frac{n_L}{\tau_L}-K^+n_{Fl}n_H\ , \quad (10)$$

$$\frac{dn_L}{dt}=-\frac{dn_H}{dt}\ , \quad (11)$$

$$\frac{dn_{Fl}}{dt}=\frac{n_d-n_{Fl}-n_L}{\tau_{Fl}}-\frac{n_{Fl}}{\tau_d}-K^+n_{Fl}n_H\ . \quad (12)$$

Equation (10) above describes the kinetics of the ensemble of carriers in the high-conductivity state. The first term of the right side of this equation is responsible for the increase in the number of carriers in the metastable state due to the decay of polarons. The rate of increase is described by the relaxation time τ_L, which is thus the mean lifetime of the polarons. The second term on the right side of Eq. (10) is the rate of flow of carriers from the metastable state to the self-trapped polaron state due to the interaction of the ensembles of carriers with the lattice fluctuations. Thus, both n_H and n_{Fl} appear, and K^+ is the relevant rate constant. Equation (11) is just the

result of the conservation law for total carrier density, $n_0 = n_H + n_L$.

Equation (12) describes the kinetics of the density fluctuations (or deformations) and its right side consists of three terms. The first term represents the available rate for new thermally induced lattice deformations. The numerator of this term is simply the density of "vacant" lattice sites where new deformations could arise. The parameter $\tau_{\rm Fl}$ is the characteristic waiting time for a fluctuation in density of the appropriate size to appear, and it can be estimated from classical statistics as $\tau_{\rm Fl} \approx \tau_0 \exp(U_{\rm el}(\Delta_{\rm cr})/k_b T)$, where $\tau_0 \sim 10^{-12}$–10^{-13} s is of the order of the period of thermal vibrations of atoms. The second term in the right side of Eq. (12) represents the decay rate of deformations after they have formed, with the appropriate relaxation time $\tau_d \sim \tau_0$. The last term on the right side of Eq. (12) describes the formation of polarons due to the interaction of carriers in the high-conductivity state with lattice deformations, with the rate of formation again being determined by the rate constant K^+.

B. Connection with the double-well potential model

The rate equations (10)–(12) will be used to describe both the electrical-conduction properties and the electrical-noise properties of Mo_2S_3. First however, it is necessary to relate the various relaxation times and rate constants to those used by Faberquist, Kirby, and Pearlstein in their phenomenological double-well model. They showed that for the double-well potential model, τ_L and τ_H were given by

$$\tau_L = \tau_{L0} \exp\left[\frac{W + E/2}{k_b T}\right], \tag{13}$$

$$\tau_H = \tau_{H0} \exp\left[\frac{W - E/2}{k_b T}\right], \tag{14}$$

where k_b is Boltzmann's constant and τ_{L0} and τ_{H0} were measured to be between 10^{-14} and 10^{-15} s. Similarly, Fagerquist, Kirby, and Pearlstein showed the equilibrium densities n_H^0 and n_L^0 to be

$$n_H^0 = n_0/[1 + \exp(E/k_b T)], \tag{15}$$

$$n_L^0 = n_0/[1 + \exp(-E/k_b T)]. \tag{16}$$

Classical statistics for a weakly interacting collection of Maxwell-Boltzmann particles (in this case, the lattice deformations) suggests that the equilibrium density of lattice deformations of sufficient size for small polarons to form will be given by

$$n_{\rm Fl}^0 = n_d \exp[-U_{\rm el}(\Delta_r)/k_b T]. \tag{17}$$

Substituting the equilibrium densities Eqs. (15)–(17) into Eq. (4) with $dn_H^0/dt = 0$, we obtain the following expression for the rate constant K^+:

$$K^+ = \frac{R^3[1 + \exp(E/k_b T)]}{\tau_{L0}[1 + \exp(-E/k_b T)]} \times \exp\left[-\frac{[W + E/2 - U_{\rm el}(\Delta_{\rm cr})]}{k_b T}\right]. \tag{18}$$

In other words, Eq. (18) provides the necessary connection between our kinetics approach with the phenomenological equations from Refs. 9 and 10, and it will be seen that our model describes all electronic properties of Mo_2S_3 studied therein, including the nonequilibrium and time-dependent conductivity and the time-dependent thermopower. Taking $E = 15$ meV and $T = 100$ K, it is seen to be a reasonable approximation that

$$K^+ \approx \frac{R^3}{\tau_{L0}} \exp\left[-\frac{[W - E/2 - U_{\rm el}(\Delta_{\rm cr})]}{k_b T}\right]. \tag{19}$$

IV. APPROACH TO EQUILIBRIUM AND THE NOISE POWER SPECTRA

Faberquist, Kirby, and Pearlstein[10] considered the approach to thermodynamic equilibrium within the framework of the double-well potential model. They assumed that the carriers transferred between two wells by thermal activation and that the transfer process was governed by Poisson statistics. In this approach, the probability $P(t_1)$ that carriers remain in the metastable (high-conductivity) state during $0 \le t \le t_1$ is given by the distribution function with a single relaxation time τ:

$$P(t_1) = \exp(-t/\tau). \tag{20}$$

Fagerquist, Kirby, and Pearlstein found direct experimental evidence for this distribution function in their pulse conductivity measurements.[10] They first passed a large current through the sample, which caused the sample temperature to rise a few degrees by Joule heating. This resulted in a redistribution of the carriers between the wells. The sample current was then reduced to a much smaller value, so that sample cooled quickly (a few ms) to near the original temperature. The conductivity $\sigma(t)$ of the sample, however, decayed slowly back to its original value $\sigma(0)$ with the disturbance from equilibrium $\delta\sigma(t) = \sigma(t) - \sigma(0)$ decaying exponentially with time according to

$$\delta\sigma(t) = \delta\sigma(0) \exp(-t/\tau_1), \tag{21}$$

where τ_1 is the experimentally measured value.

The conductivity $\sigma(t)$ is related to the density of carriers $n_H(t)$ by means of the well-known relation

$$\sigma(t) = \frac{e^2 \tau_s n_H(t)}{m^*}, \tag{22}$$

where τ_s is the carrier scattering time, e is the carrier charge, and m^* is the carrier effective mass. Note that τ_s is not in any way related to the carrier relaxation time τ_1 associated with the approach to equilibrium in the double-well potential. As can be seen from Eq. (22), the disturbance of n_H from equilibrium, δn_H, is expected to

have a similar time dependence as the conductivity, so that

$$\delta n_H(t)=\delta n_H^0 \exp(-t/\tau_1) . \tag{23}$$

From the definition of $P(t)$, it follows that the following equation should be valid:

$$\delta n_H(t)=\delta n_H^0 P(t)=\delta n_H^0 \exp(-t/\tau) . \tag{24}$$

Comparison of Eqs. (23) and (24) indicates that the Poisson distribution [Eq. (20)] agrees completely with experiment, and further that $\tau=\tau_1$. In other words, the characteristic time τ associated with the electrical noise is the same parameter τ_1, which determines the relaxation of conductivity. This result was directly demonstrated in Ref. 10. τ_1 can be determined from Eq. (10). We assume that n_H is disturbed from equilibrium by an amount δn_H, set $n_{\rm Fl}=n_{\rm Fl}^0$, and use $\delta n_L=-\delta n_H$, we obtain

$$\frac{d\delta n_H}{dt}=-\left[\frac{1}{\tau_L}+K^+ n_{\rm Fl}^0\right]\delta n_H . \tag{25}$$

The solution this equation has the same exponential form as Eq. (23) with τ_1 given by

$$\frac{1}{\tau_1}=\frac{1}{\tau_L}+K^+ n_{\rm Fl}^0 . \tag{26}$$

The substitution of Eqs. (17) and (19) into Eq. (26) yields the following expression for $\tau=\tau_1$:

$$\tau=\frac{\tau_0 \exp(W/k_b T)}{\exp(E/2k_b T)+\exp(-E/2k_b T)} . \tag{27}$$

This equation coincides exactly with Eq. (12) of Ref. 9. The Poisson distribution [Eq. (20)] of the lifetimes of carriers is known to give the following noise power spectrum:

$$S_V=\frac{4\langle(\delta V)^2\rangle\tau}{1+(2\pi f\tau)^2} , \tag{28}$$

where f is the frequency and δV is the root-mean-square voltage fluctuation due to fluctuations in the number of carriers in the high-conductivity state according to[10]

$$\delta V=-V\frac{\delta N_H}{N_H} . \tag{29}$$

Here V is the mean (dc) voltage across the sample during the electrical-noise measurements and $N_H=n_H V_{\rm Sample}$ is the total numbers of carriers in the high-conductivity state ($V_{\rm Sample}$ is the total volume of the sample). We now return to Eq. (10) and set $dn_H/dt=0$. Then the fluctuations in n_L and $n_{\rm Fl}$ must satisfy

$$\frac{\delta n_L}{\tau_L}-K^+ n_{\rm Fl}\delta n_H-K^+\delta n_{\rm Fl} n_H=0 . \tag{30}$$

Substituting ($\delta n_L=-\delta n_H$) into Eq. (27), we obtain the following equation in terms of δn_H and $\delta n_{\rm Fl}$:

$$-\frac{\delta n_H}{\tau_L}-K^+ n_{\rm Fl}\delta n_H-K^+ n_H\delta n_{\rm Fl}=0 . \tag{31}$$

Using Eqs. (13), (17), and (19), it is seen that $\tau_L^{-1}\ll K^+ n_{\rm Fl}^0$, so that the first term of Eq. (31) is expected to be much smaller than the second term. Thus we ignore the first term in Eq. (31) and it reduces to the following relation between δN_H and $\delta N_{\rm Fl}$:

$$\frac{\delta N_H}{N_H}=\frac{\delta N_{\rm Fl}}{N_{\rm Fl}} . \tag{32}$$

From Eqs. (28), (29), and (32) it follows that the noise power spectrum can be expressed in terms of fluctuations of density (or deformations) as

$$S_V(f)=4V^2\frac{\langle\delta N_{\rm Fl}^2\rangle\tau}{N_{\rm Fl}^2[1+(2\pi f\tau)^2]} . \tag{33}$$

In other words, Eq. (33) shows clearly that the deriving force for electrical noise in our small-polaron model is the fluctuation $\delta N_{\rm Fl}$ in the number of deformations which are large enough to form small polarons.

V. NOISE POWER MAGNITUDE

Following Ref. 10 we introduce the coefficient B:

$$B=4V^2\frac{\langle\delta N_H^2\rangle}{N_H^2}=4V^2\frac{\langle\delta N_{\rm Fl}^2\rangle}{N_{\rm Fl}^2} , \tag{34}$$

which is the measure of the noise power magnitude, and it is usually called the noise strength parameter. Then the problem of determination the noise power spectrum is reduced to calculating $\langle\delta N_{\rm Fl}^2\rangle$ from statistical-mechanical considerations. As mentioned before, we can neglect all the fluctuations of density with $\Delta=\Delta_{\rm cr}$ and the fluctuations are assumed to be weakly interacting. In other words, the ensemble of fluctuations with dilations $\Delta=\Delta_{\rm cr}$ or $\Delta=0$ is statistically equivalent to the ensemble of n_d particles existing in two states: the state with zero energy (corresponding to $\Delta=0$) and the state with energy $U_{\rm el}$ (corresponding to $\Delta=\Delta_{\rm cr}$). Then, the partition function Z for n_d particles distributed between two levels is[23]

$$Z=\{1+\exp[-\beta U_{\rm el}(\Delta_{\rm cr})]\}^{n_d} , \tag{35}$$

where $\beta=(k_b T)^{-1}$. The average energy $\langle U_{\rm el}\rangle$ of the ensemble is then

$$\langle U_{\rm el}\rangle=-\frac{\partial \ln Z}{\partial\beta}=\frac{U_{\rm el}(\Delta_{\rm cr})n_d}{\{1+\exp[\beta U_{\rm el}(\Delta_{\rm cr})]\}} . \tag{36}$$

But since $\langle U_{\rm el}\rangle=N_{\rm Fl}U_{\rm el}(\Delta_{\rm cr})$, this leads to

$$\begin{aligned} N_{\rm Fl}&=n_d/\{1+\exp[\beta U_{\rm el}(\Delta_{\rm cr})]\} \\ &\cong n_d\exp[-\beta U_{\rm el}(\Delta_{\rm cr})] . \end{aligned} \tag{37}$$

It can be shown that for a weakly interacting collection of Maxwell-Boltzman particles[23]

$$\begin{aligned} \langle\delta N_{\rm Fl}^2\rangle&=-\frac{1}{\beta}\frac{\partial N_{\rm Fl}}{\partial U_{\rm el}}=\frac{n_d\exp[\beta U_{\rm el}(\Delta_{\rm cr})]}{\{1+\exp[\beta U_{\rm el}(\Delta_{\rm cr})]\}^2} \\ &\approx n_d\exp[-\beta U_{\rm el}(\Delta_{\rm cr})] . \end{aligned} \tag{38}$$

Substituting the expressions for $N_{\rm Fl}$ and $\langle\delta N_{\rm Fl}^2\rangle$ into Eq. (34) gives the strength parameter:

$$B=\frac{4V^2}{n_d}\exp[U_{\rm el}(\Delta_{\rm cr})/k_bT] . \quad (39)$$

Another approach has been discussed in Ref. 10 for explaining the origin of the electric noise. In contrast with our approach, no concrete model of double potential was considered and the electric noise was simply assumed to be the result of fluctuations of number of carriers ΔN_H in the "frozen" double-well potential. The appropriate noise power magnitude B_1 calculated in this earlier approach is given by

$$B_1=\frac{4V^2}{n_0}\exp(E/k_bT) . \quad (40)$$

But the estimated value of B_1 was found to be about three orders of magnitude less than the experimental value.[10] In our opinion, the effect of electric noise turned out to be more complex than was assumed in Ref. 10. It is of considerable importance to compare strength parameter B calculated in the framework of the small-polaron model with the strength parameter B_1 from Ref. 10:

$$B/B_1=\frac{n_0}{n_d}\exp[(U_{\rm el}(\Delta_{\rm cr})-E)/k_bT] . \quad (41)$$

To estimate the value of this ratio, we choose the following experimental data:[9,10] $T=100$ K, $n_0=10^{20}$ cm^{-3}. The value of elastic energy $U_{\rm el}=0.135$ eV was taken from the adiabatic potential calculations. Using these values, the magnitude of the electric noise calculated from (41) $B/B_1=1.6\times10^3$ has the same order as measured in experiments.[10] In other words, the small-polaron mechanism can give the magnitude of the electric noise three order larger than in the model of Fagerquist, Kirby, and Pearlstein.[10]

VI. CONCLUSION

The present paper is a continuation of earlier papers where the results of experimental investigations of electronic properties and electrical noise in Mo_2S_3 were reported.[9,10] The most important unresolved issue regarding these results was to find the physical mechanism responsible which gives rise to the phenomenological double-well potential. This paper is concerned with the investigation of the acoustic small-polaron mechanism as a promising candidate for explaining all electronic properties of Mo_2S_3. We followed the approach of Toyozawa,[14] Mott and Stoneham[19] who considered small polaron as a localized carrier state accompanied by surrounding lattice distortion with the size near to atomic parameter. Kinetics equations were proposed for the derivatives of density of carriers, polarons, and lattice distortions or fluctuations of density. The kinetics constant of these equations was adjusted to the previous phenomenological approach[9,10] to describe the nonequilibrium electronic properties and parameters of the double-well potential.

Moreover, the kinetics approach allowed us to explain in a self-consistent manner the properties of electric noise and estimate its magnitude B. The estimated magnitude of the electric noise has the same order as was measured in experiments[10] and this fact, perhaps, justifies our polaron model. The previous attempt to calculate the magnitude of the electric noise on the base of a "frozen" double-well potential without taking into account the kinetics of fluctuations of density gave B three orders smaller than the experimental value.[10] It should be noted that we used in our theory only known parameters of Mo_2S_3 like the Fermi energy E_F, the effective mass m^*, the density of carriers n_0, and the atomic parameter R. These parameters were successfully used in the framework of the polaron model to estimate the energy barrier $W=0.13$ eV between two states in a double-well potential model that is not far from experimental data $W=0.25$ eV.[9,10] These results suggest that the small polaron model may satisfactorily explain the electronic properties of Mo_2S_3.

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