And erson localization and electrical 1/f noise in lanthanum strontium vanadate

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Anderson localization has been investigated in $La_{1-x}Sr_xVO_3$ for $0 \le x \le 0.4$. The results of transport studies are analyzed in terms of the pseudogap theory for localization. The conduction studies are supported by electrical 1/f noise and Hall-mobility measurements.

I. INTRODUCTION

The electrical properties of $La_{1-x}Sr_xVO_3$ change from those of semiconductor to a metal as the Sr^{2+} content is increased with a nonmetal-metal transition occurring at x=0.23. The transition has been characterized as an Anderson transition with hopping conduction at low temperature.¹ The incorporation of Sr^{2+} ions at La^{3+} sites leads to a disorder arising from a random distribution of these sites including Anderson localization of carriers in the material. High-temperature transport studies show the association of a mobility edge with the transition.² Measurements of conductivity and thermopower showed a uniform transition from semiconducting to metallic behavior as the strontium content is increased.

The transition in $La_{1-r}Sr_rVO_3$ has been characterized as an Anderson transition^{1,3} and its conduction properties have been investigated over wide ranges of temperature and frequency. The material showed variable-range hopping and ac conducitivity at low temperatures. While general conduction behavior conforms to that predicted for a simple Anderson model, some variations have been noted. The variation of activation energy with composition makes it difficult to distinguish between the behavior expected for an Anderson model and that arising from percolation effects. The theory predicts a density of states smaller than that estimated from the Sr^{2+} concentration, implying that interpretation in terms of pairs hopping is suspect.

In order to obtain a better understanding of the conduction process in the materials with Anderson localization, information concerning the density of states is necessary. This paper reports investigations of 1/f noise and Hall mobility in $La_{1-x}Sr_xVO_3$. Mott proposed a pseudogap theory for such materials. In this paper an analysis based on the above theory is presented and is used to interpret the present results and earlier conductivity data.

II. PSEUDOGAP THEORY

In order to calculate the conductivity of a disordered solid, Mott evaluated the Kubo-Greenwood formula and wrote for conductivity³

 $\sigma = (\pi e^2/\hbar) z a^6 I^2 [N(E_F)]^2, \qquad (1)$

where z is the coordination number, a^3 is the atomic volume (assuming a cubic lattice), N is the number of atoms, and I is the hopping integral. Equation (1) shows that conductivity of the material is proportional to $[N(E_F)]^2$. If N(E) is less that the free-electron value, as in a "pseudogap," the conductivity is given by

$$\sigma = S_F e^2 a g^2 / 12 \pi^3 \hbar, \qquad (2)$$

where g is defined as

$$g = N(E_F) / [N(E_F)]_{\text{free}}$$
(3)

It is the value of g that determines the nature of conduction in these materials.

The dependence of conduction characteristics on the value of g has been reflected in other studies on disordered solids,^{4,5} and we thought it would be of interest to study this in detail. Two experimental techniques have been considered. The Hall effect appeared to be a powerful tool but it is found experimentally that the Hall mobility in amorphous materials is small and is often less than the estimated drift mobility. The sign of the Hall coefficient is often anomalous and may not be the same as that of the charge carrier. Thus the Hall effectprovides a complex probe of a low mobility system. The other method is to measure the electrical excess or 1/f noise. It has been suggested that the noise power spectra provides a more sensitive average over different possible conduction paths than is reflected by the conductivity.⁶ This would imply that noise measurements provide information not available through conventional conduction studies. The following sections describe the investigations of 1/f noise and Hall mobility togeth-

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er with a discussion in relation to the conduction mechanism.

III. EXCESS OR 1/f NOISE

Excess or 1/f noise is well established as a general bulk effect in materials and is inversely proportional to the total number of charge carriers. Hooge⁷ suggested an empirical relation based on dimensional reasoning for the spectral noise power $S_i(f)$ as

$$S_{i}(f) = (\alpha/N_{f})\Delta f/f, \qquad (4)$$

where I is the current through the sample, N_f is the total number of free carriers, Δf and f being the bandwidth and the frequency of measurement, respectively. α is an empirical constant with a value of 2×10^{-3} .

1/f noise has been observed in very thin metal films, semiconductors, and glasses. With a few notable exceptions, the measured noise power in these materials is well expressed by Eq. (4). Hooge and Hoppenbrouwers⁸ studied the noise in continous gold films and scmiconductors and concluded that the noise was a bulk effect and arises from fluctuations in carrier mobility. Main and Owen⁹ measured the noise in chalcogenide glasses and made an attempt to interpret the results in terms of transport properties. Voss⁶ studied the 1/f noise in different systems and concluded that homogeneous materials can be well described by a linear mechanism. Also a strong dependence of the 1/f noise on conduction characteristics was suggested. While extensive data show that 1/fnoise is an equilibrium property, the spectrum lacks frequency-dependent spatial correlation that is characteristic of fluctuations in a diffuse medium.

In the present paper an attempt is made to relate noise properties to the conduction mechanism. The previous models considered the 1/f spectrum as a generation recombination spectrum with a relaxation time τ and a statistical weight inversely proportional to τ . The usual explanation was a variation of McWhorter's¹⁰ theory of charge trapping. 1/f noise measurements have been carried out on metal-oxide-semiconductor (MOS) devices.¹¹ The conduction in these devices occurs either within localized or extended states and the Fermi level can easily be adjusted with the application of a gate voltage. We felt it would be of interest to study the noise spectra of a bulk material which is characterized by an Anderson transition, viz., conduction occurs initially through localized states and then by band conduction in the extended states.

Current-induced 1/f noise has been measured in

small samples of pure and strontium-doped lanthanum vanadate. The preparation of this material has been described in an earlier paper.¹ The method of measurement was similar to that of Voss and Clarke.¹² The experimental technique was to measure the total spectral noise power with a constant current I applied to the sample. The background noise spectrum was then measured with zero current in the sample and the difference between these values gave the current-induced noise in the sample. The noise was amplified by a narrow band lock-in-analyzer (Ithaco 393) and measured after rectification by a precision rmsdc converter (Burr-Brown 4341). This voltage was recorded by a Fabritek 1062 instrument computer which also provided accurate analog to digital conversion and storage over a range of frequencies. Successive counts were stored to provide an average measure of the noise power spectrum. The noise power spectra were calibrated by measuring the Nyquist noise level of known resistors. The spectral noise power $S_i(f)$ was expressed in terms of noise current fluctuations as

$$S_i(f) = \Delta I^2 / I^2, \tag{5}$$

where ΔI is the measured noise current and *I* is the current through the sample. The samples were bars 0.01 cm² in area and 1 cm long. They had a resistance inversely proportional to the thickness. Reversal of bias current and variation of surface area to volume ratio failed to show any contact effects.

The noise power spectra showed a frequency dependence which was of the form

 $S_i(f) \propto f^{-\beta}$,

where β was $\simeq 0.9$ for all compositions. At 1 KHz the magnitude of the excess noise was several orders of magnitude larger than the thermal noise in the absence of a current. Measurements at 100 Hz in a bandwidth of 1 Hz have been used in the present paper. Figure 1 shows the spectral noise power at two different temperatures for different compositions of $La_{1-x}Sr_xVO_3$. A decrease in observed noise power takes place in the vicinity of the Anderson transition at x = 0.23. The figure also shows the variation of conductivity as a function of composition. The power spectrum may be analyzed using Hooge's empirical relation (4). The variation of the total number of free carriers, N_f , as a function of composition is shown in Fig. 2. The figure also shows the total number of carriers which are expected to be present on the basis that a V^{4+} ion is introduced for each Sr^{2+} subsititution of La³⁺. The carrier concentration for undoped $LaVO_3$ was determined earlier² by extrapolation from doped materials and has not been previously



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FIG. 1. Variation of spectral-power intensity as a function of composition of $La_{1-x}Sr_xVO_3$. The figure also shows the variation of conductivity over the same composition range; \bullet -300 °K; \blacksquare -195 °K; \blacktriangle -conductivity at 300 °K.

verified by an independent technique. The value of α was taken as 2×10^{-3} and the agreement of noise measurements with the conductivity suggests that impurity scattering may be absent and that the noise is generated only by the lattice scattering.¹³

The value of N_f shows an increase at the composition corresponding to the transition. The measurement would imply that delocalization takes place as x approaches 0.2 as expected for an Anderson transition and the number of carriers participating in the noise process increases. The temperature variation also suggests that the material for



FIG. 2. Number of free carriers as a function of composition: \bigcirc -300 °K; \triangle -125 °K; \diamond -estimated from conductivity measurements at 300 °K.

 $x \leq 0.2$ behaves as a semiconductor. In a conventional extrinsic semiconductor, conductivity is independent of frequency and depends on temperature through a change in the number of carriers in the valence band. When Sr^{2+} is introduced in the host material, a tail of localized states extends from valence band into the band gap and conductivity arises when carriers are excited into a band of states at the mobility edge.¹ At high concentration of Sr²⁺, a broad band of fully compensated impurity states may overlap the tail of localized states resulting in a mixed conduction. Cohen et al.¹⁴ suggested that for the overdoped case, the free carrier population will be in equilibrium with the carriers trapped in the localized states. The noise spectrum of such a system will not show any variation with either composition or temperature. This is clearly evident from Fig. 2. Voss¹¹ has also observed similar results in MOS devices.

There is a striking agreement between the value of carrier concentration in LaVO₃ measured from noise spectral power and that determined from conductivity. The basis for the conductivity calculation was that an intrinsic carrier concentration associated with oxygen vacancies in addition to carriers introduced by doping could be recognized. The independent measurement of carrier concentration from noise power spectra supports this assumption. However, the fact that $N_{\rm free}$ $>N_{\rm total}$ in the metallic regime is not understood. It corresponds to a 1/f noise power less than that predicted by Hooge relationship.

As outlined in Sec. II, the conduction properties of a material which is localized can be explained by the factor g given by

$$g = [N(E)]_{\text{total}} / [N(E)]_{\text{free}}.$$

The conduction properties of such materials will depend on the precise value of g. For the present case g=0.1 in the metallic region in which case conduction at low temperatures is by thermally activated hopping whereas at higher temperatures carriers will be excited from the nonlocalized states. This is in conformity with the observed conduction behavior of the material.

IV. HALL EFFECT

The Hall mobility is disordered solids is small and its value is often less than that estimated from drift mobility. The nature of Hall mobility for electrons and holes in amorphous materials was discussed by Friedman¹⁵ and Emin.¹⁶ The systems usually contain several types of disorder but the Anderson model which takes into account the cellular disorder is used here. Electronic motion is then assumed to be diffusive, with charge carriers performing a random walk motion from site to site. The mean path is of the order of lattice spacing and any phase information is lost over this distance. It was shown that Hall mobility depends upon local lattice geometry and is only weakly temperature dependent, whereas the conductivity mobility is temperature dependent. The theory also predicts that the Hall coefficient is smaller in magnitude than is predicted by conductivity estimates. Friedman¹⁵ uses a modification of Kubo formula and obtains for the ratio of Hall mobility $\mu_{\rm H}$ to conductivity mobility μ_c as

$$\mu_{H}/\mu_{c} = (6kT/J)\eta \overline{z}/z^{2}, \qquad (6)$$

where z is the coordination number, \overline{z} is the average number of closed site paths about an arbitrary site, and η is a constant.

The measurement of Hall mobility in disordered solids requires a very sensitive technique for the measurement of the effect. In the present work a double ac method involving simultaneous variation of electric and magnetic fields is used. The experimental system consisted of a magnet capable of delivering field strengths up to 500 kG (peak to peak). The sample current was supplied by another oscillator. The Hall signal was detected by a lock-in amplifier and fed to an instrument computer in order to obtain an enhanced S/N ratio. Measurements were carried out in four probe configuration and the system sensitivity was 0.05 cm² V⁻¹ sec⁻¹. A theoretical estimate² of the Hall mobility to conductivity from Eq. (6) gives

$$\mu_{\rm H}/\mu_c \simeq 0.1.$$

Also the conductivity mobility in bulk samples of $LaVO_3$ was found to be 0.15 cm² V⁻¹ sec⁻¹. No Hall mobility could be recorded with the present setup, implying that it is much below the sensitivity of the system. This is also in conformity with the theoretical predictions and hence an alternative technique like electrical 1/f noise was found to be useful to determine the same.

V. DISCUSSION

The addition of strontium to $LaVO_3$ results in the formation of V⁴⁺ centers and a subsequent decrease in the ion separation. This is reflected in the conductivity and reduced activation energy as the Sr²⁺ content is increased. For sufficiently large values of Sr²⁺ content, the activation energy will disappear and the disorder due to random positions of atoms

Measured	g ²	
Parameter	Theoretical	Experimental
Conductivity	0.078 ¹	0.1001
Hall effect	0.1	• • •
1/f noise	• • •	0.08
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can lead to localization. If the conduction and the valence bands overlap slightly, a "pseudogap" or minimum density of states is expected.³ As long as the overlap is small, the density of states is localized. At sufficiently low temperatures, $N(E_F)$ is finite but the states are localized near the Fermi energy. It is then that the phenomenon of variable range hopping sets in and the conductivity can be well described by a $T^{1/4}$ behavior. Sayer *et al.*¹ investigated the conduction in $La_{1-}Sr_VO_3$ and found the behavior described above in the low-temperature region. As the Sr^{2+} content is increased, a point will be reached at which the states at E_F are no longer localized. At this point a metal-nonmetal (MNM) transition of Anderson type takes place and the conductivity σ is given by

$$\sigma = Ce^2/\hbar^2 a$$

where C is a constant. Inserting experimental values of conductivity $(100 \ \Omega^{-1} \text{ cm}^{-1})$ and a (8 Å), C may be estimated as

 $C = 0.0329, g^2 = 0.1,$

which are in reasonable agreement with the pseudogap theory for Anderson localization. Table I shows the value of g obtained from various investigations which are all in conformity with the above theory.

It can be seen from Table I that the MNM transition in $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ can be well described by the pseudogap theory with the conductivity proportional to $N(E_F)$.² The analysis is further supported by thermopower measurements. The thermopower in such materials should be a maximum for compensated samples, decreases with increasing Sr^{2+} content, and then changes sign at the transition. This is in accord with experiment.²

It can be concluded from the above investigation that the conduction in lanthanum strontium vanadate can be described by the pseudogap theory for localization.

- ¹M. Sayer, R. Chen, R. Fletcher, and A. Mansingh, J. Phys. C <u>8</u>, 2059 (1975).
- ²J. B. Webb and M. Sayer, J. Phys. C <u>9</u>, 4151 (1976). ³N. F. Mott, *Metal Insulator Transitions* (Taylor and
- Francis Ltd., London, 1974).
- ⁴N. F. Mott, Philos. Mag. <u>19</u>, 835 (1969).
- ⁵M. J. Sik and R. P. Ferrier, Philos. Mag. <u>29</u>, 877 (1974).
- ⁶R. F. Voss, Phys. Rev. Lett. <u>40</u>, 913 (1978).
- ⁷F. N. Hooge, Physica B <u>83</u>, 14 (1976).
- ⁸F. N. Hooge and A. M. H. Hoppenbrouwers, Physica <u>45</u>, 386 (1969).
- ⁹C. Main and A. E. Owen, Phys. Status Solidi A<u>1</u>, 297 (1970).
- ¹⁰A. L. McWhorter, *Semiconductor Surface Physics*, edited by Ed. R. H. Kingston (Pennsylvania U.P.,

Pennsylvania, 1957).

- ¹¹R. F. Voss, IBM Research report, RC6684, Aug. 1977 (unpublished).
- 12 R. F. Voss and J. Clarke, Phys. Rev. B $\underline{13},\,556$ (1976). 13 F. N. Hooge and L. K. J. Vandamme, Phys. Lett. A $\underline{66},\,$
- 315 (1978).
- ¹⁴M. H. Cohen, H. Fritzsche, and S. R. Ovshinsky, Phys. Rev. Lett. <u>22</u>, 1065 (1969).
- ¹⁵L. Friedman, in *Electronic and Structural Properties* of Amorphous Semiconductors, edited by P. G. LeComber (Academic, New York, 1973), p. 363.
- ¹⁶D. Emin, Proceedings of the Seventh International Conference on Amorphous and Liquid Semiconductors, edited by W. E. Spear (University of Edinburgh, 1977), p. 249.