NONLINEAR CONDUCTION OF ZnS IN STRONG ELECTRIC FIELDS

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Electric conduction of cubic ZnS crystal was investigated in the field range from 2×10^4 to 3×10^6 V/cm. The resonant type current anomalies were observed around 4×10^5, 1×10^6, and 1.4×10^6 V/cm. The experimental results suggest that the Stark ladder will play an important role in the high-field transport phenomena.

Since Wannier predicted the existence of a Stark ladder arising from the motion of a Bloch electron in a periodic potential,[1] experimental[2] and theoretical[3] studies on this problem have been made especially in the fields of tunneling, electro-optical effect, and nonlinear conduction. However, it is not yet certain how Wannier's quantum state will contribute to the electrical properties of solids.[4] The purpose of this paper is to propose a possible mechanism of quantum transport due to the Stark ladder on the basis of experiments recently made in ZnS crystal.

According to Wannier, the energy separation between adjacent Stark levels is given by eEd, where e is the electronic charge, E is the electric field strength, and d is the lattice spacing. An electron in a quantum state l will be scattered into another one, l', by emitting or absorbing phonons via electron-phonon interaction.[5] The transition probabilities of the emission and absorption processes are proportional to $n_{\vec{q}}+1$ and $n_{\vec{q}}$, respectively. Here, $n_{\vec{q}}$ is the population of phonons with wave vector $\vec{q}$. The net component arising from the surplus of those processes is a spontaneous one. Therefore, the electron will be scattered into the lower lying quantum level by emitting a phonon spontaneously. In position space, this process will correspond to the transition of the electron wave packet centered at the lattice point $-ld$ to the adjacent one $(-l+1)d$, and the succession of this process will cause a stationary electric current in a crystal. If the interaction with the longitudinal optical mode is predominant, and the wave number dependence of the phonon energy $\hbar\omega_0$ is neglected, the current increase due to this effect will be expected to occur at the electric field $E_n=\hbar\omega_0/ned$. Here, n is a positive integer, and is given by $|l-l'|$. Cubic ZnS crystal seems appropriate to investigate such a problem, because of its simple band structure[6] and interband configuration.[7] According to the measurements of Raman scattering,[8] the $\hbar\omega_0$ value is estimated to be about 0.04 eV. When the electric field is applied along [111] direction, one obtains $E_1=4.6\times10^5$, $E_2=2.3\times10^5$ V/cm, and so on.

Experiments have been carried out on ZnS thin films deposited by vacuum evaporation.[9] First of all, aluminum as an electrode was evaporated on a quartz plate, then ZnS 3 mm in radius was evaporated on the aluminum, and finally a counter electrode of aluminum with 1.5-mm radius was evaporated. The temperature of the substrate was maintained at about 500°K in the ZnS evaporation process. Under this condition, the samples were cubic, and had a preferred orientation along [111] axis.[10] The thickness of the sample was measured by a shift of the resonance frequency of the quartz plate. Gold wires were attached to the aluminum electrodes by conducting silver coating material. Electric conduction was studied, in a vacuum of 5×10^{-6} Torr, by using a dc-voltage pulse whose width and repetition rate were 3×10^{-6} sec and 100 Hz, respectively. The current was of the order of 10^{-5} A at the field of 10^5 V/cm. The sampling process was effective in order to obtain a good signal-to-noise ratio. All the measurements were made at room temperature.

A typical example of the conductivity ratio σ/σ_0 versus electric field is shown in Fig. 1. Below 1.5×10^5 V/cm, σ/σ_0 keeps a constant value, which shows the Ohmic relation. Above 1.5×10^5 V/cm, the curve begins to deviate from the Ohmic relation, and increases with increasing the electric field strength. The deviation from Ohm's law seems to be classified into two types. One is a monotonic deviation of the base current, and the other is the resonant-type anomaly around 4×10^5, 1×10^6, and 1.4×10^6 V/cm. The intensity and the width of the anomalous component are estimated to be about 10% of the base component and about 1×10^5 V/cm, respectively. Although the characteristic field values were somewhat scattered, similar results were observed in about twenty samples used in the measurements. Figure 2 shows curves of σ/σ_0 vs E for three different samples with poor preferred crystal orientation.[11] The σ/σ_0 value is nearly proportional to $\exp\sqrt{E}$, and no resonant-type anomaly is ob-

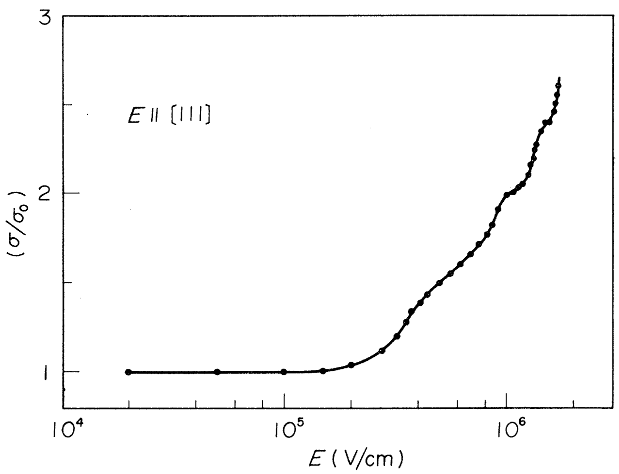

FIG. 1. A typical example of conductivity ratio versus electric field. σ_0 is the low-field conductivity. Thickness of the sample is 1.6×10^{-4} cm. The error of each point was estimated experimentally as 2% both in the ordinate and the abscissa. The absolute value of the electric field was estimated within 10% accuracy.

served. This relation suggests that the field-assisted internal emission known as the Poole-Frenkel effect[12] is a predominant conduction mechanism for the monotonic deviation observed in Fig. 1. Figure 3 shows the angular variation of the relation between σ/σ_0 and E.[13] The anomalies are clearly seen for the [111] field direction, while they become smaller and finally disappear with increasing the angle between [111] and the field direction. This suggests that the intensity of the resonant-type anomaly will depend on the field direction. A possibility that we are seeing barrier breakdown phenomena[14] seems remote because the better the crystalline state, the larger the anomaly. The voltage-controlled negative resistance has been observed in very thin-film insulators,[15] in which the phenomenon is voltage dependent, and thickness independent. Our data will not fit such phenomena. The Gunn effect has been observed in ZnSe and CdTe,[16] whose energy band is similar to that of ZnS. Our samples, however, are too thin to be composed of a high-field domain. This situation will also rule out the possibility of a piezoelectric instability. The successive ionization of electrons from discrete trap levels will not account for the results shown in Fig. 3.

It is suggested that the resonant-type current anomaly may be related to the quantum effect mentioned above. The anomaly observed around 4×10^5 V/cm seems to correspond to that estimated at $E_1 = 4.6\times10^5$ V/cm. The fact that no observation of the anomaly was found around E_2 or lower fields is well understood provided that the broadening of the quantum level is larger than the eEd value at such small electric fields. This is not inconsistent with the observed linewidth of about 1×10^5 V/cm. The results in Fig. 3 will also be supported by this picture, because

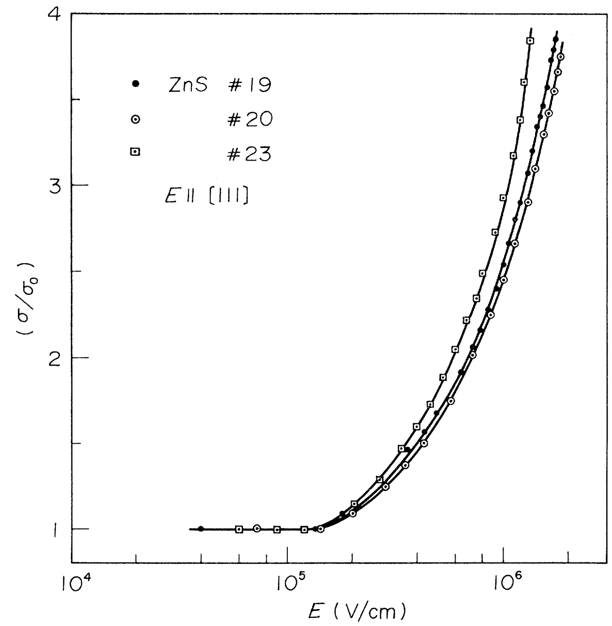

FIG. 2. Examples of the Poole-Frenkel–type current conduction.

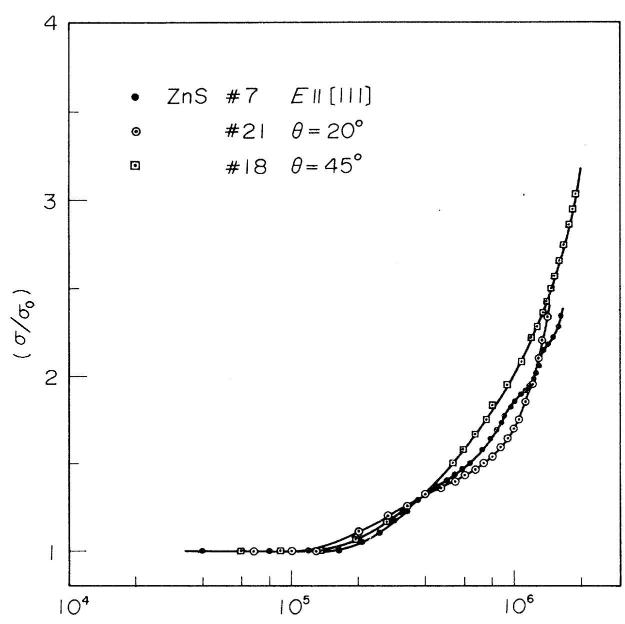

FIG. 3. The angular dependence of conductivity ratio versus electric field for three samples. θ is the angle between the [111] axis and the electric field direction.

Wannier's levels are not expected for an arbitrary direction of the electric field. On the other hand, the observations around 1×10^6 and 1.4×10^6 V/cm are not expected from a one-phonon process. These seem to correspond to eEd values 2 and 3 times larger than the phonon energy, which suggests two- and three-phonon processes. It is natural to consider that the transition probability for multiple-phonon processes will be smaller than that for a one-phonon process. However, the number of electrons capable of contributing to the periodic motion will increase with increasing electric field strength. The current anomaly is concerned with the product of these effects. This situation will give rise to rather large anomalies around 1×10^6 and 1.4×10^6 V/cm. The multiple-phonon process may well be expected in our case, because a similar effect was observed in phonon-assisted tunneling phenomena in polar[17] and nonpolar[18] semiconductors. The acoustical phonons with wave vector near the zone boundary will also contribute to the anomaly. However, the energy of the acoustical phonons is small,[8] and these will contribute to the broadening of the anomaly. The q dependence of the optical mode will also give rise to the broadening effect. In conclusion, our results suggest that the resonant-type current anomaly comes from the quantum effect.

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[7]The energy separation (3.7 eV) between the valence and the conduction band is larger than the conduction bandwidth (2 eV) between the Γ_1 and L_1 points. At the L point, the separation between lower and upper conduction bands is large (3 eV).

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[9]Wannier's level is well understood in a one-dimensional case. The thin film will give rise to a one-dimensional conduction.

[10]It has been reported that the preferred orientation is [100] when deposited on cleaved NaCl. See V. K. Miloslavskii, Fiz. Tekh. Poluprov. 1, 629 (1967) [Soviet Phys. Semicond. 1, 527 (1967)].

[11]These samples were obtained when the temperature of the substrate was maintained at room temperature in the evaporating process.

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[13]In this measurement, the angle between [111] axis and the field direction was controlled by inclining the substrate in the evaporating process.

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