hibit quite different characteristics. These produce a radiation pattern which is almost uniform in the azimuthal plane, but which is only a few tenths of a degree wide in the vertical plane, as shown in Fig. 1(d). This pattern implies that there is coherence over a distance of the order of 100 μ in the vertical direction but virtually no spatial coherence in the horizontal direction.

While stimulated emission has been observed in many systems, this is the first time that direct conversion of electrical energy to coherent infrared radiation has been achieved in a solid state device. It is also the first example of a laser involving transitions between energy bands rather than localized atomic levels.

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ELECTRONIC CONDUCTION OF POLYMER SINGLE CRYSTALS

A. van Roggen
Engineering Department, E. I. du Pont de Nemours & Company, Wilmington, Delaware
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Electronic conduction at high current densities has been observed in single crystals of linear polyethylene placed between two metal electrodes. The crystals[1] are placed broad side down on a metal substrate which functions as an electrode, while the second electrode consists of a catwhisker. The two electrodes are connected to a zero-impedance power supply[2] with an x-y recorder for plotting the voltage-current graphs. Typical crystals have an area of 10×20 μ^2 and it is necessary to work under a high-power microscope. Contact pressure and area cannot be kept constant over long periods. Nevertheless, reproducibility of the I-V curves is good for individual crystals on a copper substrate, though fluctuations in thickness and growth of the crystals give rather large variations in the experimental data taken from different crystals. Shorts between catwhisker and substrate show up as straight, nonrectifying I-V curves characteristic of a small residual resistance in the connecting wires and catwhisker.

Figure 1 shows the I-V characteristic of a 100Å polyethylene crystal between Pt catwhisker and Cu substrate (Pt/Cu). At low voltages the curve shows a small rectification ratio with the larger slope in the first quadrant, where a region of negative resistance is found at increased field strength. The same general shape of the I-V curve is observed for Mo or W catwhiskers, but W/Cu has opposite rectification compared to Pt/Cu and Mo/Cu, and current increases with the difference of the metal's contact potential relative to that of copper in air. On most other metal substrates, the visibility of the crystals is not high enough for proper positioning of the catwhisker. However, experiments have been made on the system Au/Au with a 100Å crystal and similarly shaped curves were found with peak voltage and current at lower values (about 60 mV and 10 μA). The gold for substrate and catwhisker may have slightly different contact potential due to differing impurities and to the etching treatment necessary in sharpening the

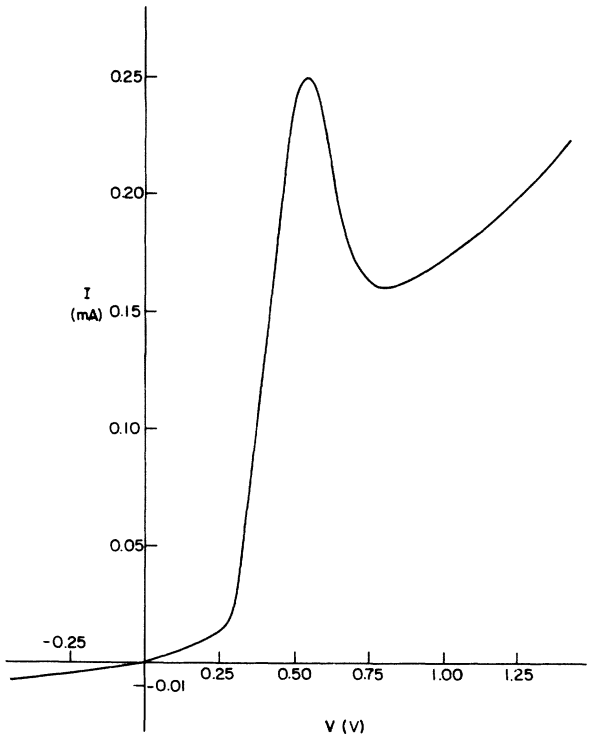

FIG. 1. I-V characteristic of a 100Å polyethylene single crystal between Pt catwhisker and Cu substrate.

catwhisker, but its use eliminates explanations based upon oxide layers.

Figure 2, curves 1, 2, and 3 show the systems Pt/Cu, Mo/Cu, and W/Cu with a 100Å crystal. Curve 4 shows a reduction in current density in Mo/Cu resulting from recrystallizing the polyethylene[3] to a fold length of 300-400 Å, and a decrease in peak voltage resulting from a change in contact potential of the whisker due to differing surface treatment in the sharpening process. If, on the other hand, the 100Å crystal is replaced by a crystal consisting of two stacked layers of 100 Å each as occurs near a spiral dislocation, or equivalently, by two overlapping independent crystals, the current density not only decreases even further, but more importantly the region of negative resistance vanishes (curve 5).

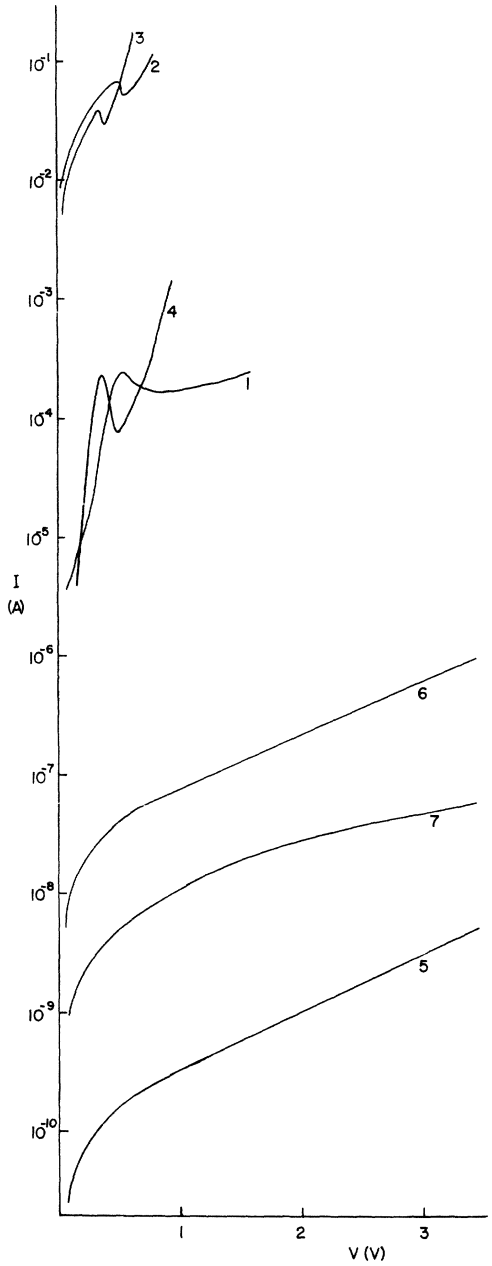

FIG. 2. Curve 1: Pt/Cu with 100Å crystal. Curve 2: Mo/Cu with 100Å crystal. Curve 3: W/Cu with 100Å crystal. Curve 4: Mo/Cu with 300-400Å crystal. Curve 5: Pt/Cu with stacked layers of crystals. Curve 6: Pt/Cu with nitrocellulose film. Curve 7: Pt/Cu with electron-irradiated polyethylene crystal.

In order to compare polyethylene crystals with other materials, thin films of nitrocellulose were measured under the same experimental conditions. These amorphous films (curve 6) give *I-V* plots comparable to those of overlapping polymer crystals. Different film thicknesses and contact pressures give graphs of the same shape but displaced along the *I* axis. The curves show features similar to those reported for charge tunneling through vacuum or Al_2O_3 barriers between metals.[4] Crystalline barriers such as thin vacuum-deposited films of Ge do not show negative resistance regions, and even those polyethylene crystals that normally show *I-V* graphs such as curve 1 can act as normal tunneling barriers: Curve 7 is observed in Pt/Cu after irradiating the crystals with a low dose of high-energy electrons. Electron micrographs demonstrate that the crystal morphology is unchanged by the low radiation dose. The major part of the radiation-induced changes is localized in the fold planes of the crystals because internal crosslinking is negligible compared to crosslinking between compactly stacked crystals.

It appears that the anomalous behavior displayed by the upper curves of Fig. 2 is a result of surface effects. In these crystals the molecular chains are perpendicular to the broad faces and are folded at those surfaces. The crystal can thus be divided into two surface layers of about 5 to 10Å thickness that contain the chain folds, and an inner region with the parallel, straight-chain segments. The crystal is highly anisotropic[5]: The projected distance between two adjacent CH_2 groups parallel to the *c* axis (and the electric field) is 1.3 Å, while that to the closest neighbor in the *ab* plane is 4.5 Å. Polyethylene has a low carrier mobility and in the crystal surface layers the electron wavelength is larger than both the free path length and the thickness of the layers. Furthermore, the applied field strength is in the order of 10^6 to 10^7 V cm^{-1}, where nonlinearity in the *I-V* curve arises due to strong field emission[6] or similar effects. The usual band theory approximations therefore have

to be applied with caution. Nevertheless, a tentative model is proposed for the conduction which is consistent with the experimental results. Ionic current can be ruled out because the number of monovalent charge carriers needed in typical experiments exceeds by many orders of magnitude the number of crystal lattice points in the current path. Space-charge-limited currents are reported to cause dc negative resistance,[7] but the experiments described here are not limited to dc; at 20 cps the anomalous behavior is still observed, and moreover, the current decreases with crystal thickness much faster than the third power.[8] This strong dependence of current on thickness and the region of negative resistance are suggestive of current tunneling which is observed between degenerate p and n semiconducting regions[9] and between superconductors.[10]

The tentative model for the systems studied here describes the inner region of the crystal as a perfect lattice with large energy gap, and the outer layers as thin imperfect crystals consisting of the chain folds. The energy states of these layers are ionized by metal electrodes, depending upon the contact potential, and hence act as injector electrodes.

The current through the single crystal consists of two main parts: on one hand, tunneling from catwhisker to substrate through the whole crystal, and on the other hand, charge injection from the catwhisker into the surface states, tunneling through the perfect part of the crystal into the opposite surface states and finally into the metal substrate. If the applied voltage lowers the energy levels in the surface layer adjacent to the substrate to a position equal to or lower than the energy levels in the surface layer at the catwhisker, then the second part of the current will be enhanced and give rise to a negative resistance region. For any given crystal, the peak voltage will be determined by the difference in contact potential at the two surfaces while the total current depends upon the difference in barrier height; i.e., the energy level difference between the inner part of the crystal and the surface states.

When the current passes through two single crystals in series, a decrease in total current density and a decrease of the negative resistance effect is consistent with the model described. The two contacting surface layers form an area with strong carrier scattering and thus can be described as an energy barrier of considerable height. As the transmission coefficient of a barrier is exponentially dependent upon the barrier height, it follows that the current through two crystals is smaller than that through a single crystal of the same total thickness. Furthermore, as the total current is given by the product of the transmission coefficient and the density of surface states in the layers near the metal electrodes, the effect of the current leading to the region of negative resistance is reduced simultaneously.

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NEGATIVE SURFACE FREE-ENERGY EFFECTS IN SUPERCONDUCTING NIOBIUM*

T. F. Stromberg and C. A. Swenson
Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa
(Received September 17, 1962)

The transition metals such as niobium, vanadium, and tantalum have been classified in the past as "hard" superconductors, since they customarily exhibit irreversible magnetization curves, locked-in flux and broad superconducting transitions.[1] This type of classification is quite arbitrary, however, since the work of Ittner, Budnick, Seraphim, and others has shown that tantalum exhibits soft rather than hard superconducting behavior if it is made sufficiently pure.[2-7] There is no reason to believe that tantalum is unique in its behavior, and a similar relationship between sample purity and superconducting properties should exist for other transition metals. Very roughly, the procedure which was used in the treatment of the tantalum samples was first to obtain the highest purity raw metal available, and then to degas the samples by heating them close to the melting