$d(\Delta n_a)=d(\Delta n_c)=-\frac{1}{2}d(\Delta n_b)$. Suppose that transition c is saturated by an rf signal, $\Delta n_c \rightarrow 0$. In thermodynamic terms, transition c is placed in thermal contact with a heat source whose temperature is essentially infinite. The spin temperature of c will thereupon be heated to infinity. Transition c is also in heat contact with transitions a and b via the cross-relaxation process. The final equilibrium conditions for a and b must be predicted by maximizing the total entropy, subject to the cross-relaxation constraints.

If Δn_a and Δn_b have the same initial value Δn_0, the relationship between them at any time is $\Delta n_b=3\Delta n_0-2\Delta n_a$. The first two terms in the entropy expression can be written with Δn_b eliminated as

$$S=-\tfrac{3}{2}(k/N)[5\Delta n_a{}^2-12\Delta n_0\Delta n_a+9\Delta n_0{}^2].$$

Maximizing this expression against Δn_a yields

$$\Delta n_a=6/5\Delta n_0, \quad \Delta n_b=\tfrac{3}{5}\Delta n_0.$$

Sorokin et al. predicted this same result from the rate equations. They also experimentally verified the 20% increase in absorption on a and the 40% decrease on b when c was saturated.

An example in which a multilevel spin system with harmonic cross-relaxation between levels is initially perturbed and then allowed to come to equilibrium has also been analyzed by the author, using the same approach. The results show, as one would certainly expect, that the system comes to a new equilibrium in which a Boltzmann distribution prevails among the cross-relaxing levels.

SUMMARY

An approximate expression for spin-system entropy in terms of the population differences has been given. The expression is useful in finding the final equilibrium conditions in cross-relaxation experiments without needing the cross-relaxation rate equations.

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Comparison of Structures of Surfaces Prepared in High Vacuum by Cleaving and by Ion Bombardment and Annealing*

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A comparison has been made for a bismuth telluride crystal of the structure of (0001) surfaces produced by cleaving in high vacuum, with similar surfaces prepared by the ion-bombardment and annealing technique. The low-energy electron-diffraction patterns of the two surfaces were found to be similar and of approximately the same intensities. Only integral order beams were present. It is concluded that both methods produce essentially clean surfaces with the same atomic arrangements, in the case of this crystal.

I. INTRODUCTION

THE method of ion bombardment and annealing developed by Farnsworth et al.,[1] has been extensively used for cleaning surfaces in high vacuum, particularly for nonrefractory substances where heat treatment alone is ineffective. Important evidence that surfaces so produced, under carefully monitored conditions, are atomically clean has been obtained from low-energy electron-diffraction measurements of the cleaned surfaces.[2]

An additional method of producing clean surfaces on bulk single crystals is that of breakage or cleavage in high vacuum. At room temperature the method is obviously more suitable for brittle materials, for example most semiconductors. Comparatively large cleavage faces can be obtained on cleaved and fractured surfaces of various semiconductors.[3] Such surfaces can be assumed to be largely clean if there is negligible contamination from the surrounding low-pressure ambient, or from diffusion of impurities from the uncleaved sides of the specimen. It would be of interest, however, to make measurements, for a particular crystal, on known crystallographic surfaces produced both by cleaving and by ion bombardment and annealing. Since the structures of the surfaces might conceivably be affected by either treatment, low-energy electron-diffraction tests of the surface structures are of particular interest.

Such a comparison has been carried out for bismuth telluride, a semiconductor of rhombohedral structure type $R\bar{3}m$. Regarded as a hexagonal lattice, ready cleavage is observed along (0001) planes, perpendicular to the hexagonal axis. Experiments were made on this material because it cleaves more readily than most semiconductors, a mechanical feature of importance for

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[1] H. E. Farnsworth, R. E. Schlier, M. George, and R. M. Burger, J. Appl. Phys. **26**, 252 (1955).

[2] H. E. Farnsworth, R. E. Schlier, M. George, and R. M. Burger, J. Appl. Phys. **29**, 1150 (1958).

[3] D. Haneman, J. Phys. Chem. Solids **11**, 205 (1959).

cleavage experiments in a high-vacuum electron-diffraction tube.

II. EXPERIMENTAL TUBE AND CLEAVAGE SYSTEM

The cleavage system was built around a low-energy electron-diffraction tube (assembled by Dr. R. E. Schlier) of a type described by Farnsworth et al.[2] The cleaving mechanism is shown in Fig. 1, being similar in principle of operation to one described by Haneman.[3] It consists essentially of a hinged molybdenum rod to whose upper end is screwed a molybdenum collar carrying a rigidly attached piece of razor blade. The rod assembly rests on the spring G and is supported laterally by chromel disks separated by glass spacers. A nickel slider C can be driven by magnetic control against either of the molybdenum collars H which are screwed firmly to the rod.

For cleavage, the crystal is moved into a suitable position over the razor blade which can be positioned accurately parallel to the crystal face by rotating the rod assembly with a torque applied magnetically to D. The blade is driven into the crystal by applying magnetically controlled blows with the slider C against the upper stop H, the penetration into the crystal being about 1 mm. A tungsten rod which can be retracted into a side arm supports the crystal on the opposite side against the blow from the blade. With the blade held in the crystal, the latter is jerked backward by a magnetic pull applied to a nickel slug attached to the other end of the rod holding the crystal. This causes a segment of crystal to be flicked off, exposing a flat mirror-like cleavage surface.

After this the blade is moved out of the way by forcing the slider C down against the lower stop H, and clamping the assembly in this position by pushing the fork E over the pin I. The crystal is then moved into the electron diffraction chamber for measurements.

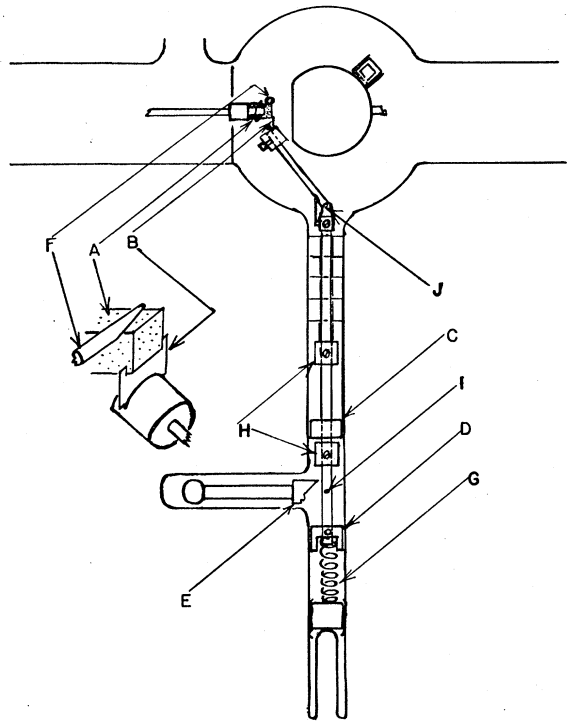

FIG. 1. Arrangement for cleaving bismuth telluride. A—crystal, B—razor blade, C—nickel slider, D—nickel "U" piece, E—nickel fork, F—retractable tungsten wedge shown in cross section, G—tungsten spring, H—molybdenum collars screwed to shaft, I—molybdenum pin through shaft, J—hinge. The assembly rests on the spring G but can be held in other positions by causing the fork E to bear on the pin I. Vertical movement of the blade is achieved by forcing the slider C against the stops H. The assembly may be rotated by applying magnetic forces to D. Details of the diffraction tube are given in reference 2.

III. CRYSTAL PREPARATION AND MOUNT

The high-purity single crystals were undoped p type. They were tetragonal in shape, with a 5-mm square front face, parallel to (0001) planes, and a length of 6 to 7 mm. Before insertion of a crystal in the tube, a fresh front face was produced by cleavage.

Two "U"-shaped molybdenum-sheet clamps, reinforced by tungsten clips, held the crystal in position, as shown in Fig. 2. The clamps were attached to a molybdenum block to whose other end was screwed a molybdenum rod. A chromel-alumel thermocouple passed through a hole in the block and made permanent contact with the back of the crystal.

IV. VACUUM PROCEDURES

All metal parts of the crystal-mount arrangement were degassed before assembly by radio-frequency heating to high temperatures in vacuum. The vacuum and gas handling system for the diffraction tube was similar to that described by Schlier and Farnsworth.[4] The experimental tube was baked for 2 days at 300°C, with traps cooled in dry ice, and subsequently the trap separating the tube from the rest of the system was cooled in liquid nitrogen. After outgassing schedules and the firing of Mo getters, pressures below 10^{-9} mm Hg were obtained.

V. RESULTS OF CLEAVAGE EXPERIMENTS

Four separate portions were cleaved from one crystal, exposing four separate cleavage faces. The results for these surfaces were the same. In the best case, a portion of the low-energy electron-diffraction pattern was recorded within five minutes of cleavage. This portion of the pattern served as a reference for detecting any possible contamination during subsequent measurements of the complete diffraction pattern. Although the pressure was initially below 10^{-9} mm, the movement of parts inside the tube during cleavage caused a momentary pressure increase up to 5×10^{-9} mm.

[4] R. E. Schlier and H. E. Farnsworth, J. Chem. Phys. **30**, 917 (1959).

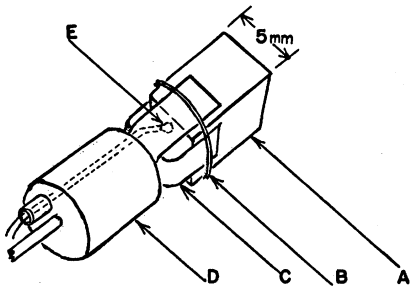

FIG. 2. Crystal Mount. *A*—crystal, *B*—tungsten clip, *C*—molybdenum sheet "*U*" pieces, *D*—molybdenum block, *E*—head of thermocouple.

VI. CONTAMINATION

The sticking coefficients for oxygen and carbon monoxide on the above surfaces were found to be very low. However the possibility that the surface might have been substantially contaminated even before the first diffraction beam was recorded was examined.

It is noted that the number of molecules in the tube envelope at a given time during the period of interest was of order 10^{11}, which is three orders of magnitude less than the number required to form one monolayer on the crystal. Hence, adsorption of as much as a significant fraction of a monolayer by the fresh surface should have caused readily detectable pressure changes. To check this, blank runs were made in which the cleavage mechanism was operated, but without the blade actually penetrating the crystal, after which the crystal was moved into the diffraction drum. It was found that the pressure rise caused by the movement of parts while going through this procedure was the same as that caused when a crystal was actually cleaved. This shows that the cleavage process did not introduce new phenomena which would cause detectable pressure changes, i.e., that there was negligible adsorption on the cleaved faces during the time of interest. This is of course consistent with the behavior noted five minutes after cleavage when any subsequent adsorption could be checked by the electron diffraction measurements.

A further possibility of contamination arises from diffusion over the surface of foreign atoms from the sides of the crystal or from the section at the edge which was touched by the razor blade. (It has previously been found that considerable atomic transfer can take place when surfaces are brought into medium-pressure contact.[5] This possibility was tested experimentally by keeping the blade in contact with the clean surface at a part near the edge for 16 hours at an elevated temperature of 50°C. No change in the diffraction pattern obtained from the central region of the surface was observed after this treatment. Theoretically, in order to cause contamination of the clean surface in the time between cleavage and the first measurements, a diffusion rate for foreign atoms of order 1 mm/minute at room temperature would be required. Such a rate would be exceptionally high even for surface diffusion.

VII. DIFFRACTION PATTERNS

Sharp intense diffraction patterns were obtained from the freshly cleaved surfaces. The nature and intensity of the beams were essentially the same for all the cleaved surfaces. In Fig. 3 is shown a plot of the positions of the beams in angle and voltage for one azimuth together with their theoretical positions, assuming that the surface atoms act as a two dimensional grating with a spacing the same as that in a bulk (0001) plane.

Two features are noteworthy. Firstly, the close agreement between the positions of the beams and the theoretical curves indicates that the surface atoms have the same spacing as in the bulk. Secondly, only integral order beams were observed, in contrast with the diamond-structure semiconductors Ge, Si[4], and InSb[6] where half- and other fractional-order beams were also found.

Tests with oxygen and carbon monoxide indicated that these gases showed negligible adsorption on the surfaces at room temperature. Water vapor had a maximum sticking coefficient of about 10^{-5}. Fuller details on adsorption are given separately.[7]

VIII. ATOMIC ORDER ON CLEAVED SURFACES

The cleaved surfaces were subjected to heat treatment to test whether appreciable disorder had been caused by the rupture that occurs during cleavage.

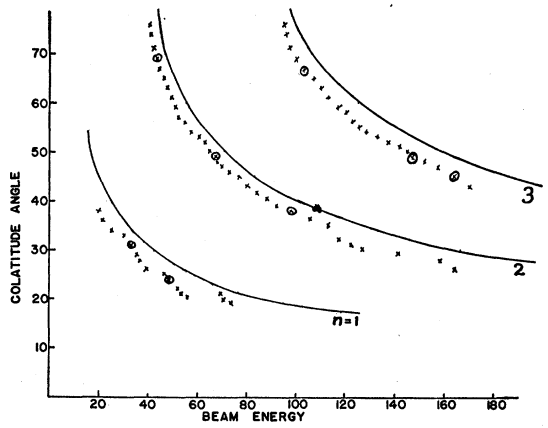

FIG. 3. Positions of diffraction beams in the $(10\bar{1}0)$ azimuth for a cleaved (0001) surface of Bi_2Te_3. Crosses (×) represent peaks in plots of collector current versus beam energy. Circles (⊗) represent positions at which the peaks are maximized. Solid curves are theoretical plots of surface grating formula $n\lambda = d \sin\theta$ using the relevant bulk lattice constant of 4.384A for Bi_2Te_3. The order of diffraction, n, is marked on the curves. The slight deviations of the experimental points from the solid curves arise because the primary electron beam was not exactly normal to the crystal face.

[5] D. Haneman and A. J. Mortlock, Proc. Phys. Soc. (London) **B70**, 145 (1957).

[6] D. Haneman, Proceedings of Second Conference on Semiconductors Surfaces (to be published).

[7] D. Haneman, following paper [Phys. Rev. **118**, 567 (1960)].

Annealing for one to two hours was carried out at 150°C, 215°C, and 250°C. After each treatment the diffraction beams were checked in several azimuths. However no significant increases ($<1\%$) in intensities of the beams were found after any of these treatments. Experiments to be described below indicate that effective annealing of ion-bombardment damage takes place at about 200°C and above. Hence, the above results indicate that although the crystal was heated above the temperature that is effective for annealing disorder among the surface atoms, the increase in order on the cleaved surface was very small, corresponding to an increase in diffraction beam intensity of less than 1%. This shows that the order among the atoms on the cleaved surfaces was high, and that the forces acting on the surfaces during rupture were insufficient to cause appreciable disturbance of the atoms. This result is not surprising in view of the comparatively low forces required to cleave bismuth telluride.

IX. ION BOMBARDMENT AND ANNEALING

The cleaved surfaces were subjected to various argon-ion bombardment and annealing cycles. The results did not appear to be sensitive to ion energies within the experimental range of 300 to 600 volts. Full precautions against the back-sputtering effect[6] were taken. Weak diffraction beams were observable even after extensive ion bombardment. For example, after bombardment at 30 $\mu a/cm^2$ for 30 minutes at 400 volts the diffraction pattern was reduced in intensity to a few percent of its original value, indicating extensive, but not complete, atomic disorder. Further ion bombardment did not cause this residual pattern to weaken, even after 8 hours of treatment at four times the current density. Such treatment was sufficient to cause visible erosion of the surface, with more than 100 microns removed.

The effects of annealing after bombardment were studied. Heating the crystal at 100°C for 23 hours had no effect on the residual pattern. Treatment at 140°C for 1 hour caused a small improvement. A sharp pattern was obtained, however, after heating at 220°C for about 1 hour. Further heat treatment to 260°C caused no further change in the pattern. Apparently the minimum temperature for effective annealing of bombardment damage is about 200°C. After these bombardment-anneal cycles the intense diffraction patterns found were closely similar to those obtained from freshly cleaved faces. The diffraction beams occurred at the same voltages and angles, and had intensities within the small range found for the cleaved faces.

Adsorption characteristics were the same as for the cleaved faces.

X. DISCUSSION

The most noteworthy feature of the above results is the close agreement between the diffraction patterns and adsorption characteristics found for cleaved surfaces and those produced by ion bombardment and annealing. The manner of producing a surface is essentially different in the two procedures.

During cleavage, although the role of dislocations is important, the determining factors are the forces between the atomic planes that are to be separated. A new surface is taken to be produced when these forces or bonds are ruptured. On the other hand, during ion bombardment, atoms on the surface are sputtered off by the impinging ions. With a material like bismuth telluride, having alternate layers of different compositions, this process may be complex. However, after the damage to the surface structure had been annealed out by heat treatment, the resulting surfaces had the same structure as those obtained at room temperature by cleavage. This agreement provides good evidence that the surface structure found by the two cleaning methods is the normal equilibrium structure of a clean surface.

Although the above results apply only to bismuth telluride, their general significance is of interest. It is noteworthy that a representative clean surface could be obtained by the ion-bombardment and annealing technique on a substance of complex composition like Bi_2Te_3. This suggests that the method may be applicable to other materials of complex composition. Although a surface largely free of distortion has been produced at room temperature by the cleavage technique, the possibility still remains that a distorted surface may be produced on other materials. This would apply particularly for substances like Ge or Si where atomic bonds stronger than in Bi_2Te_3 must be ruptured during cleavage.

XI. ACKNOWLEDGMENTS

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