The same difficulty also exists for alloys between II–VI compounds. Only moderate success in doping both $n$- and $p$-type has been reported thus far for CdTe–ZnTe[19] and ZnTe–ZnSe[20] alloys. By contrast, nearly all III–V compounds and alloys between them can be doped degenerately both $n$- and $p$-type. Thus, by forming alloys between the III–V compounds and the II–VI compounds, it may be possible to overcome the doping difficulty, while at the same time achieving the high bandgap. This seems indeed to be the case, as indicated by the present doping results of the (III–V)—(II–VI) alloys.

## IV. CONCLUSIONS

Of the 12 (III–V)—(II–VI) systems studied, three alloy systems were found to form solid solutions throughout the entire composition. These are GaAs–ZnSe, GaP–ZnSe, and GaP–ZnS. Preliminary analyses of optical absorption data in all the three systems indicated the existence of alloys having a direct gap in excess of 2 eV. The doping behavior, coupled with the optical results, of these alloys shows promise that they might provide an efficient electroluminescent source well into the visible range of the spectrum.

[19] F. F. Morehead and G. Mandel, Appl. Phys. Lett. **5**, 53 (1964).
[20] M. Aven and W. Garwacki, Appl. Phys. Lett. **5**, 160 (1964).

*Note added in proof*: While this article was in press, a paper appeared on the preparation and energy gaps of GaAs-ZnSe alloys: S. M. Ku and L. J. Bodi, J. Phys. Chem. Solids **29**, 2077 (1968). Although both papers are generally in agreement as to the sublinear dependence of bandgap on composition, their report of Vegard's law for this alloy system is at variance with the present results. It is possible that this discrepancy may be due to nonstoichiometry, as discussed in the text.

## ACKNOWLEDGMENTS

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# Effect of Pressure on Al–I–Bi Tunnel Junctions

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Measurements of resistance ($dV/dI$) versus bias ($V$) have been made for Al–I–Bi junctions at 77°K up to pressures of 30 kbar. The junctions were prepared by evaporation upon freshly cleaved mica and the pressures generated in a girdle die using AgCl as the pressure transmitting medium. The results are reversible with pressure cycling. A conduction maximum occurs at $\approx 0.13$ V and a kink at $\approx -0.15$ V. The maximum changes with pressure at a rate $dV/dP = -1.7\times10^{-6}$ V/bar. A change in the tunneling curve is observed at the semimetal to semiconductor transition.

## INTRODUCTION

Bismuth changes gradually and continuously from a semimetal to a semiconductor with increasing pressure. If tunneling characteristics, obtained for Bi–insulator–normal metal (Al) junctions, reflect the band structure of Bi, then these characteristics should change markedly if the junction is put under pressure and the Bi is converted from a semimetal to a semiconductor. Such an experiment would also give the pressure dependence of some features of the band structure of Bi. Finally, if such tunneling experiments can be performed with conventional high-pressure equipment, then some types of infrared spectroscopy become possible without the complication of optical windows in the pressure cell.

The effects of pressure on the electrical properties of bismuth may be summarized as follows: The electrical resistivity of Bi increases by about 50% in 25.4 kbar at room temperature before a crystallographic transition to the Bi II phase occurs. At 77 K Bi I transforms directly to Bi III at 37.5 kbar. Measurement of the pressure dependence of the Hall coefficient and the magnetoresistance at room temperature shows that the number of carriers decreases rapidly with increasing pressure and that the hole mobility increases sharply while the electron mobility increases only slightly.[1] Three studies of the temperature dependence of the electrical resistivity have shown that the temperature coefficient of resistivity changes sign with in-

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[1] J. R. Vaisnys and R. S. Kirk, J. Appl. Phys. **38**, 4335 (1967).

indium solder joint are extremely fragile and great care had to be taken not to pull them off during the loading operation. The high pressure die is a conventional girdle die with a 1.43 cm diam by 3.2 mm high cavity as shown in Fig. 1. The girdle was placed in a cryostat which has been described previously.[12]

It is known that AgCl is quite plastic at room temperature but that it becomes much more brittle with decreasing temperature.[13] One has the choice of either cooling to 77 K and increasing the pressure at the low temperature or of only increasing the pressure at room temperature and making a temperature cycle at each pressure. In the former, one relies on the extreme thinness of the junction so that the pressure over the sample will approach hydrostatic conditions even though the AgCl is quite brittle. Although the latter sequence minimizes the effects of the brittle AgCl, it exposes the junction to the differential thermal expansion between the mica, the junction, and the AgCl. Although we were able to temperature cycle a junction at two different pressures, advancing the pressure at 77 K proved to be more reliable. If the junction was going to fail it seemed to do so during the initial compaction of the AgCl around the junction as the pressure was increased to one or two kilobars. Consequently, the pressure was raised at room temperature to about 5 kbar and, if the junction was still intact, the system was cooled to 77 K. Out of about 15 junctions we made two successful runs, but it has since been found that there was a nonparallelity in the cryostat and this may have contributed substantially to the high rate of failure.

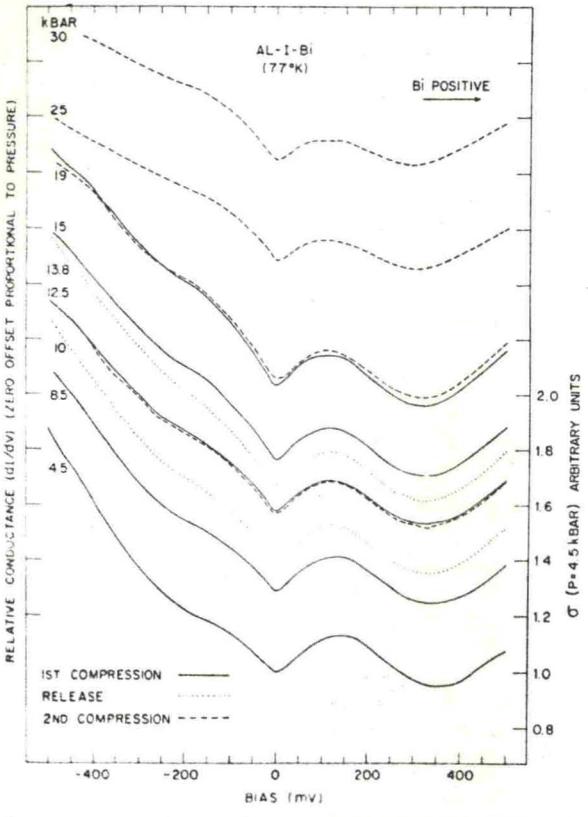



FIG. 2. The relative conductance vs bias for Al–I–Bi junctions at 77 K. The curves have been displaced so that the conductance at zero bias is proportional to the pressure.

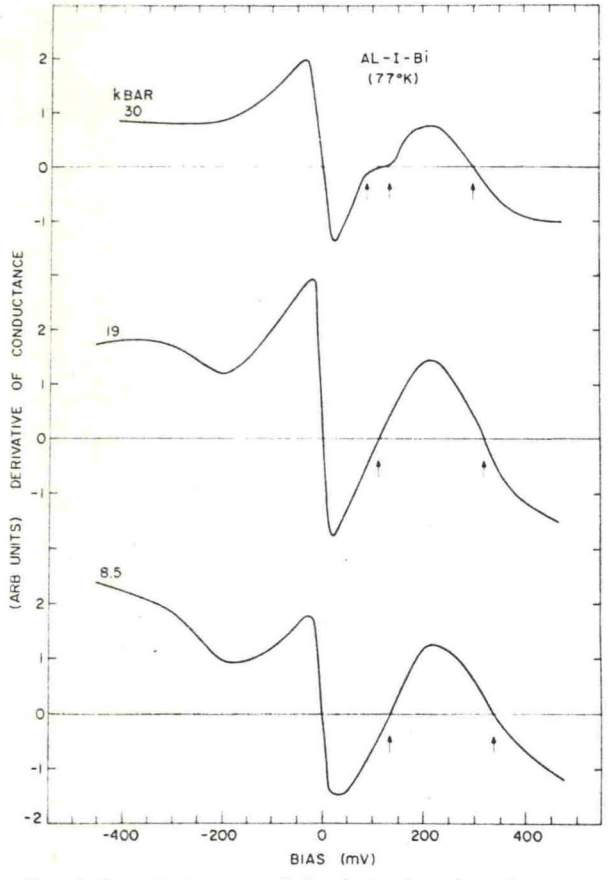



FIG. 3. Smoothed curves of the derivative of conductance vs. bias at 77 K. The bias of the conduction maximum and minimum were determined by the zeroes in the derivatives (see arrows).

The resistance $(dV/dI)$ of the junction was measured by modulating the dc bias voltage with a small constant ac current and measuring the generated ac voltage with a lock-in amplifier. The resistance vs bias curve was traced on an $x$-$y$ recorder and converted to relative conductance at 10 mV intervals. The resulting derivative curves are shown in Fig. 2. The pressure calibration is based on previous measurements of the applied load needed to reach the transition in Bi at 25.4 kbar, at room temperature, and a linear calibration was assumed. This assumption has been found to be quite good, and the observed calibration is almost the same as that calculated on the basis of the applied load divided by the area of the girdle cylinder. Tunneling characteristics were recorded at 4.5, 8.5, 12.5, 15, and 19 kbar. To test the reversibility of the measurements, curves were taken at 13.8 and 10 kbar with decreasing pressure. Tunneling characteristics were then recorded at 12.5, 19, 25, and 30 kbar during the

[12] D. N. Lyon, D. B. McWhan, and A. L. Stevens, Rev. Sci. Instr. **38**, 1234 (1967).
[13] L. C. Towle, J. Appl. Phys. **37**, 4475 (1966).

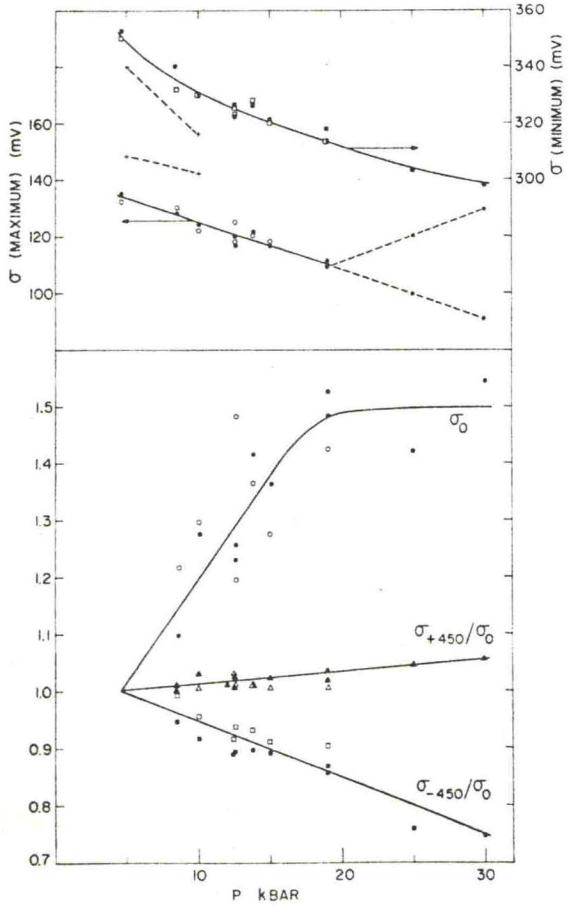



FIG. 4. Variation of the bias of the conduction maximum and minimum with pressure from experiment in which pressure advanced at 77 K. Open and closed points are for the two junction on the same mica sheet. + from experiment in which pressure increased at room temperature. (Bottom) variation of $\sigma_0$, $\sigma_{+450}/\sigma_0$ and $\sigma_{-450}/\sigma_0$ with pressure. Data normalized to curve at 4.5 kbar.

second pressure cycle. The pressure was then increased and the resistance of the Bi strip monitored. The transition from the Bi I phase to the Bi III phase in the film occurred at 37.5 kbar at 77 K, in reasonable agreement with the work of Souers and Jura. The junction was still intact after the Bi had gone through the crystallographic transition; however, the gasket of the high-pressure cell blew out before a tunneling characteristic could be obtained. It is not unusual for the gasket to fail on compression at liquid-nitrogen temperature around 50 kbar.

In order to define the maxima and minima of the $dI/dV$ curves, the second derivative was calculated by taking the slope of a straight line fit over 40 mV intervals. The computer generated curves for three different pressures are shown in Fig. 3. The extrema are defined by a zero in the derivative of the conductance as shown by the arrows. In Fig. 4 the positions of the extrema are plotted as a function of pressure. The open and closed points are for the two junctions on the same mica plate. Also included are the two points obtained on a junction in which the pressure was increased at room temperature and temperature cycles made at each pressure. Also plotted are the relative change in the conductance at zero bias ($\sigma_0$), and the ratios of the conductances at +450 mV and −450 mV to $\sigma_0$. All the measurements are normalized to the values at 4.5 kbar. These curves include the points obtained both on compression and release.

## DISCUSSION

The analysis of the data obtained at high pressures must be somewhat speculative because there are a number of serious questions about the interpretation of atmospheric pressure tunneling phenomena. The first of these questions is: What structure in the tunneling characteristic does one take to locate the energy of a band edge? The second is: Why, in all the tunneling work to date on polycrystalline films, and in Giaever's results on single crystals,[7] does one not observe the low-energy band edges which are the only ones known with some certainty from other work? We will discuss these questions briefly, not because we have any answers, but in the hope of stimulating further thought on the subject.

Tunneling between normal metals (as opposed to semiconductors) has to date proved remarkedly unproductive. As shown by Harrison, as long as the tunneling takes place into one band, the tunneling conductance is independent of the density of electron states in that band.[11] In fact from the bismuth results we can say that the over-all conductance is independent of the total density of electrons; this is inferred because Al–I–Bi and Al–I–Pb junctions prepared in the same way have similar conductances although the electron densities differ by $10^5$. Thus in the case of normal metal tunneling we expect any bias dependence of the conductance to be dominated by changes in the shape of the tunneling barrier. This distortion of the barrier gives rise to a conductance approximately described by

$$G=\alpha+\beta V+\gamma V^2+\cdots. \qquad (1)$$

where $\alpha$ is the constant conductance commonly associated with tunneling at low voltages.[14] The terms $\beta V+\gamma V^2+\cdots$ appear as a roughly parabolic conductance dependence with a minimum which is offset from zero bias by $-\beta/2\gamma$.

In general, the voltage dependence of the conductance for our junctions resembles that reported by Hauser and Testardi at one atmosphere pressure, although some structures are smeared in our case. They found that the conductance could be described by an offset parabola on which were superimposed a number of peaks in conductance.[8] By measuring the optical absorption of the films, they concluded that the band edges in Bi are resolved in tunneling as maxima in conductance.

[14] J. M. Rowell, in *Tunneling Phenomena in Solids*, E. Burstein and S. Lundqvist, Eds. (Plenum Press, Inc., New York, 1969).

i.e., the point of maximum deviation from the background parabola. This is a somewhat surprising result because a model calculation by Ben Daniel and Duke for tunneling at a band edge shows that, although the exact conductance-voltage dependence changes with the approximations used to describe the barrier, the band edge itself is marked by an inflexion in conductance or discontinuity in $dG/dV$.[15]

The second question regarding the significance of our atmospheric pressure data may well be more serious. The band structure of bismuth is well known for energies near the Fermi level; there are four band edges within 40 mV of the Fermi level.[16] These band edges are not observed in the conductance plot of Hauser and Testardi or in our data. Hauser and Testardi reported[5] that reproducible structure was observed in $d^2I/dV^2$ vs $V$ at $+30$ and $-22$ mV. Presumably the top of a hole band above the Fermi level would show a different shape in $d^2I/dV^2$ from the bottom of an electron band above the Fermi level. We considered the possibility that these edges are obscured in our data by the rather strong dip in conductance that occurs from about $-100$ to $+100$ mV (it is also hard to explain this dip as a density of states effect). To examine our data more critically we plotted the odd conductance $[G^+(V)-G^-(V)]/2$ vs $V$[$G^+(V)$ is the conductance for the Bi positive bias, $G^-(V)$ for Al positive bias at the same voltage]. This plot is a convenient way to eliminate the roughly symmetrical dip in conductance about $V=0$ from the data. (In the absence of any other effects, this plot should give the term $\beta V$ from equation (1) directly). Band edges, we believe, should be observed as inflexions in this odd conductance. Our data does show some very weak inflexions but their sign does not agree satisfactorily with the known band structure of bismuth nor are they entirely reproducible from junction to junction. We are forced to conclude that the low energy bands in bismuth are not observed in our polycrystalline films using tunneling.

Despite the difficulties outlined above, in order to interpret our data obtained at high pressure, we will proceed to follow the assignment used by Hauser and Testardi, namely, that peaks in conductance locate the band edges. We hope that the questions raised above will encourage further theoretical consideration of what conductance structure might be expected for tunneling into band edges in Bi and further experimental work, especially on single crystal Bi of various orientations. Hopefully the atmospheric pressure result will be understood more completely in time and it may then be necessary to reexamine the effects of pressure reported here.

[15] D. J. Ben Daniel and C. B. Duke, Phys. Rev. **152**, 683 (1966).
[16] G. A. Antcliffe and R. T. Bate, Phys. Letters **23**, 622 (1966) and references therein.

The derivative curves of Figs. 2 and 3 show several notable features. The most obvious in Fig. 2 is the distinct change in the over-all shape of the conductance between 19 and 25 kbar. This corresponds to the pressure at which the semimetal to semiconductor transition is expected. At this transition we would expect an energy gap to appear at $V=0$ which would have a width of $<10$ mV at 30 kbar. As $kT$ smearing of the characteristic at 77 K is $\sim 20$ mV it is reasonable that this energy gap is not resolved. We would not expect any dramatic changes in the higher energy bands at this transition and the modification of the conductance at high voltages between 19 and 25 kbar is surprising. It is possible, of course, that this is due to changes in the aluminum oxide barrier. As the pressure dependence of conductance in aluminum oxide junctions using an electrode other than bismuth has not been investigated this question cannot be resolved at present.

At 25 and 30 kbar the conductance maximum, which we do associate with the bismuth film, has broadened and gives the appearance of splitting into two peaks. Fig. 3 shows that the pressure dependence of the maximum below 25 kbar would extrapolate linearly with one of the peaks, if the maximum is assumed to split into two peaks at 25 kbar.

The over-all background tunneling conductance ceases to be parabolic at the higher pressures. As indicated previously, the background of the tunneling characteristic should be a parabola, usually displaced from zero bias, if it is controlled principally by the insulating layer. It is possible to fit our data at 4.5 kbar with a reasonable parabola, but at higher pressures ($\approx$10 kbar) any fit becomes physically unreasonable. Again this may result from changes in the aluminum oxide layer rather than in the bismuth.

The pressure coefficient of the position of the conductance maximum is $-1.7\times10^{-6}$ eV/bar. The overlap in energy of the conduction and valence bands of Bi at 1 atm is about 0.03 eV. If the critical pressure for the uncrossing of the bands is 25 kbar, then the pressure coefficient for the shift of one band relative to the other would be $-1.2\times10^{-6}$ eV/bar, similar to the coefficient for the conduction maximum above.

In conclusion, we have made successful measurements of the tunneling characteristics of Al-I-Bi tunnel junctions to 30 kbar at 77 K. A change in the characteristic curve is observed at the semimetal to semiconductor transition. A feature which is tentatively associated with a band edge in Bi is found to move with pressure at a rate of $-1.7\times10^{-6}$ V/bar.

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