ters <u>13</u>, 390 (1964).

²U. Valdrè and M. J. Goringe, J. Sci. Instr. <u>42</u>, 268 (1965).

³R. Gevers, P. Delavignette, H. Blank, and S. Ame-

linckx, Phys. Status Solidi (Germany) <u>4</u>, 383 (1964).
⁴R. Gevers, P. Delavignette, H. Blank, J. Van Landuyt, and S. Amelinckx, Phys. Status Solidi (Germany), 5, 595 (1964).

TUNNELING IN LEAD SALT *p*-*n* JUNCTIONS

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Hall¹ has observed structure near zero bias in the conductance-voltage curves of tunnel p-n junctions at 4.2°K in 11 different semiconductors. More recently, two of these materials (Ge and Si) have been studied near 1°K,² and similar effects have been observed in metal-oxide-metal diodes.³ In spite of these observations, a clear theoretical explanation for them is still not available. For this reason, we have made extensive experimental measurements on three semiconductors (PbS, PbTe, PbSe) to temperatures near 1°K. We have observed two striking effects not previously reported, and have studied their temperature and magnetic field dependence.

The p-n junctions were made by alloying dots into the host crystal. Indium dots were used on p-type PbS and PbTe while a (Sn-In) dot was used on PbSe.⁴ These junctions were immersed in liquid helium which could be pumped to near 1°K. The current *I*, resistance dV/dI, and second derivative of voltage d^2V/dI^2 were directly plotted as functions of voltage with an *X*-*Y* recorder. The differentiator used has been described previously.⁵ The ac sensing signal in the differentiator was adjusted so that even the data at the lowest temperature were not distorted by the sensing signal. A typical peak-to-peak sensing voltage was 100 μ V.

In Fig. 1, the resistance, dV/dI, of three lead salt diodes is plotted against voltage (directly from recorder traces) for different temperatures. The normalizing resistance of the background, R_b , is the resistance at zero bias at the lowest temperature, T_b , at which structure is not observed. The main features of Fig. 1 can be summarized as follows: At T_b , the resistance is a smooth function of the voltage for all three samples. As the temperature is decreased below T_b , the resistance near zero bias increases markedly. The increase in resistance is symmetric about zero bias when the resistance at T_b is also symmetric about zero bias. The common feature of the data is that all three diodes exhibit a strongly temperature-dependent resistance near zero bias. Consider now the differences in the data.

In Fig. 1(a) (PbS), there is a bell-shaped resistance at 4.2°K. This is termed a Λ curve. The broken line is the 4.75°K curve shifted to coincide at large bias with the 4.2°K curve. It shows that the bell is just superimposed on the smooth background. The 4.2°K curve is similar to those observed previously near 1°K.^{2,3} However, the 1.36°K curve shows a symmetric dip (undershoot) below the shifted 4.75°K curve. Correspondingly, this is called a W curve. Recently, this type of undershoot has also been observed in InSb.⁶ The maximum effect is a resistance increase of about 30%.

In Fig. 1(b) (PbSe), there is a much larger undershoot and also some additional structure in the curve. Notice that the position of the structure shifts with temperature. The undershoot is plainly visible at 4.2° K, and the maximum resistance increase is about 70%.

Finally, in Fig. 1(c) (PbSe) at 4.2° K, spikes (marked with arrows) are observed. They are symmetrically located about zero bias. The original data at this temperature are reminiscent of the 1.37° K data in Fig. 1(b) in that both show similar spikes. On decreasing the tem-



FIG. 1. The resistance R(V) (normalized to the zerobias background resistance, R_b) plotted against bias for three typical lead salt tunnel junctions at the temperatures indicated. T_b is the washout temperature for the effect.

perature to 1.38°K two changes are observed: The resistance increases, and the voltages at which the spikes occur shift with temperature. The strength of the spikes is considerably increased as the temperature drops. These spikes have been found to be sensitive to magnetic fields. More will be said about this later. This particular diode is also of the *W* type, although the spikes mask out the undershoot in zero magnetic field.

It is believed that the W shape is an intrinsic

junction property. Previous conclusions^{1,7} that the undershoot was probably due to a surface or edge effect seem erroneous in light of the new low-temperature data presented here and junction etching studies.

The effect of temperature on the resistance at zero bias has been studied in some detail. In Fig. 2, the normalized resistance increment $\left[\Delta R/R_{h} = R(V=0)/R_{h}-1\right]$ is plotted as a function of temperature. Since a heuristic model³ predicts a logarithmic temperature dependence for the incremental conductance, the resistance data have been converted and plotted in this fashion as well. As seen, the resistance curve can be fitted by two straight lines while the conductance curve cannot be fitted in any simple way. The experimental data were also plotted in four additional ways to determine whether any other simple fits could be found. The conclusion reached from the six plots was that the two-segment $\log T$ behavior in Fig. 2 was the only simple empirical description for the experimental results.

These results are surprising in light of the very good conductance fits obtained previously.^{2,3} First, since no theory exists it is not obvious how data should be presented. By de-fault, we have compared our data with the phenomenological model of Wyatt,³ which explicitly assumes a temperature-independent back-



FIG. 2. A plot of the normalized resistance increment $\Delta R/R_b$ and the normalized conductance increment $\Delta G/G_b$ against logT for the PbSe junction 12-10. Points obtained from different runs are indicated in the $\Delta R/R_b$ plot.

ground through Eq. (2). The significance of background and its temperature dependence has not yet received careful consideration. Experimentally, there is a finite background shift. Because of the lack of a theory, we are forced, therefore, to eliminate data with any appreciable background shift, even though background shift may be implicit in the final explanation of the effect. In order to compare data with any temperature-independent background model, we need a quantitative measure of the distortion of the data from agreement with the model caused by temperature variations in the background. The percentage distortion in a $\Delta R/R_b$ (or $\Delta G/G_b$) plot due to a shift in the background with temperature is [100(1)] $(+1/\epsilon)/(1+1/\delta)$]%, where ϵ is the fractional shift in $\Delta R/R_b$ (or $\Delta G/G_b$) and δ is the fractional change in R_b (or G_b), both taken between the two temperatures being considered.

Using this formula, let us consider the previously reported experimental data along with that being presented here. In the metal-oxidemetal junctions,³ the background does not shift with temperature ($\delta = 0$), so that there is no problem in comparing the data with any temperature-independent background model. For the p-n junctions analyzed by Logan and Rowell,² $\delta = 0.04$, $\epsilon = 0.04$, and $\Delta T = 3.2^{\circ}$ K. From the above equation, there is a 100% uncertainty or distortion in the location of the lowest temperature data point. Therefore, it is not possible to compare these data with a model such as Wyatt's. In our case, $\delta = 0.01$, $\epsilon = 3.8$, and $\Delta T = 2.9^{\circ}$ K, so that the maximum uncertainty is less than 2%.

Once it has been determined whether the experimental data can be reduced for comparison to a temperature-independent background model, the question of which model to consider and how properly to verify it arises. In the metal-oxide-metal junction case, the particular model selected was a phenomenological one having a logarithmic temperature dependence for the incremental conductance. Unfortunately, we find that the original nine data points give straight line fits on three additional kinds of plots $[\Delta R/R_b, \log(\Delta R/R_b), \text{ and}$ $\log(\Delta G/G_h)$ vs $\log T$]. The fits are equally good with the same nine points, so much so that it is impossible to discriminate between them. Because the effect is too small (13 to 20%), the temperature range too limited (8 to 1.5° K),

and the number of data points (nine) too few, verification of the model was not really achieved. On the other hand, our data were found to violate Wyatt's conductance model. In fact, the only <u>simple empirical</u> description for the experimental results is the two segment $\log T$ dependence of the incremental resistance as in Fig. 2. The break is real and was not caused by instrumentation. The points shown were taken on different immersions in the bath and on different days, to give some idea of the scatter. Similar curves (two straight line segments) have been seen on five other lead salt diodes. None of the units fits Wyatt's conductance model.

The results obtained (and some additional magnetic field data) will now be summarized: (1) New voltage structure has been found in the form of spikes which split in a magnetic field. These spikes (seen out as far as 30 meV), are not an integral part of the shape of the W curve. The primary evidence for this is that these spikes can be extinguished magnetically while the W shape remains. Magnetic field studies with the field oriented in the plane of the junction show that, typically, the resistance W at 14 kG is decreased to 15% of its zero field value, but the essential W character is still present and only a faint trace of one or two spikes remains. Splitting of the spikes is generally observed in much lower fields of about 1 to 2 kG. (2) Based on the lower temperature, magnetic field, and etching studies, it has been concluded that the resistance undershoot (Wcurve) is an intrinsic junction property of the three lead salts PbTe, PbSe, and PbS. Very large resistance changes at zero bias of up to 380% have been observed. The origin of this effect may not be the same one which causes the structure seen by Wyatt³ or by Logan and Rowell.² Our data are quite similar to results obtained with superconductor-normal metal diodes,⁸ and this is because the alloyed dots are superconducting when we observe the Weffect. (3) The previously observed temperature dependence offered as evidence for Wyatt's density-of-states model has been shown to be ambiguous in the metal-oxide-metal samples for which it was originally suggested. Further experiments on those samples will be needed to resolve the ambiguity. The data for the p-njunctions in Ge and Si² cannot be taken as support for the model because of uncertainty due to background shift. In our diodes which have

a small background shift (1%), the data do not agree with the model. (4) Empirically, it has been found that in the lead salts, the incremental zero-bias resistance exhibits a two-segment logarithmic temperature dependence.

Finally, the spikes and the lack of fit to Wyatt's model are characteristic not only of lead salt diodes but also of III-V diodes.⁹ If the effects being observed here are explainable within the present framework of tunneling theory,¹⁰ then at low temperatures the measured conductance is the product of the density of states and the tunnel probability. Although previous tunnel phenomena have been interpreted as density-of-states effects, we cannot eliminate the tunnel probability on the basis of existing data. Both the smooth effects and the spike resonance spectroscopy are being pursued experimental-ly and theoretically.

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¹R. N. Hall, <u>Proceedings of the International Confer-</u> <u>ence on Semiconductor Physics</u>, <u>Prague</u>, <u>1960</u> (Academic Press, Inc., New York, 1961), p. 193.

²R. A. Logan and J. M. Rowell, Phys. Rev. Letters <u>13</u>, 404 (1964).
 ³A. F. G. Wyatt, Phys. Rev. Letters <u>13</u>, 401 (1964).

³A. F. G. Wyatt, Phys. Rev. Letters <u>13</u>, 401 (1964). ⁴We would like to acknowledge our gratitude to R. N. Hall and J. Racette for generously providing these diodes and for a number of private communications.

 $^5W.$ R. Patterson and J. Shewchun, Rev. Sci. Instr. 34, 1704 (1964).

⁶R. A. Logan, private communication.

⁷R. N. Hall and J. H. Racette, J. Appl. Phys. <u>32</u>, 2078 (1961).

⁸M. Strongin, A. Paskin, O. F. Kammerer, and M. Garber, Phys. Rev. Letters 14, 362 (1965).

⁹J. Shewchun and R. M. Williams, to be published. ¹⁰J. Bardeen, Phys. Rev. Letters <u>6</u>, 57 (1961); and

W. A. Harrison, Phys. Rev. <u>123</u>, 85 (1961).

BAND POPULATION EFFECT ON THE INTERBAND FARADAY ROTATION IN SOLIDS: PbS

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The presence of a strongly temperature-dependent "paramagnetic" contribution to the Faraday rotation associated with localized centers in a magnetic field has long been recognized.^{1,2} This contribution arises from the thermally induced difference in population between the ground and low-lying excited states of the system from which the left- and rightcircularly polarized transitions (lcp and rcp) originate. More recently, strongly temperature- and carrier concentration-dependent contributions to the interband rotation have been observed experimentally in the semiconductors PbS^{3,4} and GaSb.⁵ In these materials, the interband rotation reverses sign at some low temperature. This temperature increases with increasing free carrier concentration. An explanation for this reversal in terms of the difference in the Burstein-Moss edge shift for lcp and rcp radiation has been given for PbS⁴ and suggested for GaSb.⁶ An additional feature of this effect which has not been recognized previously is that the interband rotation is modified by the free carrier population in such a way as to approach a finite value at low frequencies, in contrast to the interband rotation in insulating solids which approaches zero at zero



FIG. 1. Measured Faraday rotation in n-type PbS including both interband and free carrier contributions.