FIG. 1. Energy distributions of photoelectrons from Au. For this photocathode the photoelectric current saturated at a retarding potential of zero volts, so that no correction for contact potential was necessary. An estimate of the maximum electron energies from the current-voltage saturation curves for the 833 A and 704 A radiation indicated a work function of approximately four ev for this sample.

the Fermi band. The vertical arrows on the 833 A and 704 A curves indicate the lowest electron energy which would be expected from the surface photoelectric effect on the basis of a simple free electron model.

Figure 2 presents electron energy distributions for an "untreated" Ge photocathode. Units similar to those of Fig. 1 were used in Fig. 2. As in the case of Au, an abundance of low-energy electrons was observed. For Ge the maximum in the 1216 A curve at 2.3 ev was particularly sharp compared to that for Au.

The essential difference between the distributions observed at photon energies near the photoelectric threshold[4] and those at higher photon energies is the
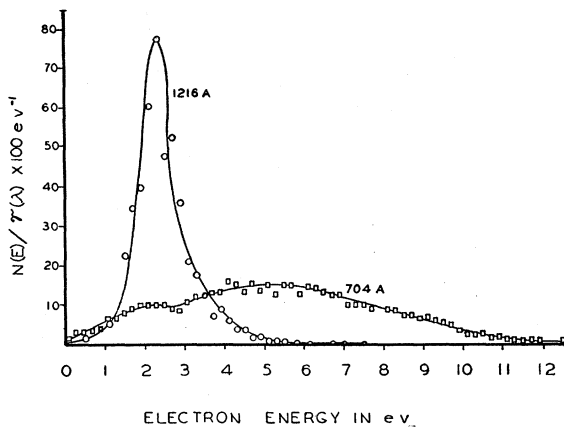

FIG. 2. Energy distributions of photoelectrons from Ge. The photoelectric current saturated at a retarding potential of +2 volts indicating the presence of a contact potential between the photocathode and the spherical collector. A correction has been made for this in determining the electron energies. An estimate of the maximum electron energies from the current saturation curves gave a work function in this case of the order of 2 to 3 ev. This low value of the work function indicated that the Ge surface was contaminated, probably with absorbed gases.

extremely small number of photoelectrons emitted with energies near the maximum energy in the latter case. A possible interpretation of this effect is that for large photon energies the electrons are released within the volume of the material,[2] undergo multiple electron scattering and thus emerge with greatly reduced energies.

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X-Ray and Neutron Diffraction Study of Ferroelectric PbTiO₃†

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DESPITE the considerable experimental and theoretical work accomplished on ferroelectric $BaTiO_3$, the crystal structure of the tetragonal phase remains unsolved. The atomic positions in the tetragonal pseudo-perovskite cell are: Ba at $(0, 0, 0)$; Ti at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+\delta z_{Ti})$; O_I at $(\frac{1}{2}, \frac{1}{2}, \delta z_{OI})$; O_{II} at $(\frac{1}{2}, 0, \frac{1}{2}+\delta z_{OII})$ and $(0, \frac{1}{2}, \frac{1}{2}+\delta z_{OII})$. An x-ray study, by Kaenzig,[1] assumed $\delta z_{OII}=0$, and gave $\delta z_{Ti}=+0.014$ and $\delta z_{OI}=-0.032$. In a subsequent detailed analysis, Evans[2] concluded that the interaction between coordinate and thermal oscillation parameters precluded a unique structure determination by x-rays. He gave the most reasonable parameters as $\delta z_{Ti}=+0.012$, $\delta z_{OI}=-0.026$, and $\delta z_{OII}=0$; but he stated that a model with $\delta z_{Ti}=+0.015$, $\delta z_{OI}=-0.024$ and $\delta z_{OII}=-0.020$ also gave good agreement except for quite unreasonable temperature corrections. In both of his models, O_I was shifted in a direction opposite to the shift in Ti; and in the second model the two O_{II} atoms moved almost the same distance, and in the same direction, as O_I, but again opposite to the Ti shift. In this second model, one could consider the cubic oxygen network to be only slightly distorted, and thus to be more or less fixed in the tetragonal lattice with respect to the nonferroelectric cubic structure,[3] and regard the Ti and Ba ions as shifting in the same direction, but with Ti moving farther than Ba.

That $PbTiO_3$ is isomorphous with $BaTiO_3$ has been shown by a phase-diagram study of $(Ba, Pb)TiO_3$.[4] Whereas the tetragonal distortion in $BaTiO_3$ is small, with $c/a=1.01$ (and $a=3.986$ A), the distortion in $PbTiO_3$ is much larger since its $c/a=1.063$ (with

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$a=3.904$ A). This larger distortion in $PbTiO_3$ permits resolution of 1, 0, 0 and 0, 0, 1 reflections even in a neutron powder diffraction pattern; and it suggests larger ion shifts, which might facilitate a structure determination by x-rays. We have consequently undertaken x-ray and neutron diffraction analyses of $PbTiO_3$, both in order to solve the tetragonal $PbTiO_3$ structure itself, and if possible to shed some light on the tetragonal $BaTiO_3$ structure.

Single crystals of $PbTiO_3$ were grown by the method of Rogers.[5] A single-domain crystal 0.04×0.04 mm² in cross section was used for x-ray intensity measurements. $(h01)$ intensity data were collected using the multiple film technique, and with Mo $K\alpha$ radiation filtered through Zr foil. Structure factors showed best agreement with $\delta z_{Ti}=+0.041$, $\delta z_{OI}=\pm0.11$, $\delta z_{OII}=\pm0.11$, and with a temperature parameter $B=0.57$ A². The possible $+$ or $-$ signs of both δz_{OI} and δz_{OII} result in four models for which the discrepancy factors $R=\Sigma|(|F_0|-|F_c|)|/\Sigma|F_0|$ all lay between 0.053 and 0.057. (R for all $\delta z=0$ was 0.16.) It was not possible, consequently, to decide between the four models on the basis of the available x-ray intensities.

It should be pointed out here that a decision between models with δz_{OI} and δz_{OII} positive and/or negative has never been made in the case of the previously published $BaTiO_3$ x-ray studies. Models with δz_{OI} negative and δz_{OII} either zero or negative have been examined, but no analysis of a model with δz_O's positive has been published.

At this point in the study, neutron powder diffraction data were collected at the Brookhaven reactor, on material prepared at The Pennsylvania State University. Ceramic pellets were fired at 1000°C, and were then finely powdered. A specimen 1.25 cm thick was irradiated by a beam 5 cm high and 2.3 cm wide, with a wavelength of 1.08 A. As can be seen in Table I, a comparison of observed neutron intensities with calculated neutron intensities for the four models shows clearly that the only satisfactory model is that with $\delta z_{OI}=+0.11$, $\delta z_{OII}=+0.11$, and $\delta z_{Ti}=+0.041$. Observed neutron intensities are compared with calculated intensities for nine peaks, involving eleven sets of lattice planes. Calculations are also shown for a model with all δz values$=0$.

Since the calculated (1, 0, 0) and (2, 0, 0) reflections must be the same for all five models, $[I_{(1,0,0)}^{(calc)}+I_{(2,0,0)}^{(calc)}]$ was scaled to $[I_{(1,0,0)}^{(obs)}+I_{(2,0,0)}^{(obs)}]$ for all the models. Values of $I_{hkl}^{(obs)}-I_{hkl}^{(calc)}$ are given in parentheses. The agreement with the model with all δz values positive is striking; and the other models are clearly less satisfactory. It is not possible to account for either the x-ray or neutron scattering under the assumption that $\delta z_{OII}=0$.

The equivalent δz values for O_I and O_{II}'s suggest that the oxygens in $PbTiO_3$ be considered as "fixed" in the lattice, the cubic oxygen octahedra above the Curie

Table I. Observed and calculated powder diffraction intensites for $PbTiO_3$ for five models, in integrated counts per 0.1 minute; figures in parentheses$=I_{hkl}^{(calc)}-I_{hkl}^{(obs)}$.

		I_{hkl}(calc)				
		δz_{Ti}: $+$ δz_{OI}: $+$ δz_{OII}: $+$	$+$ $-$ $-$	$+$ $+$ $-$	$+$ $-$ $+$	0 0 0
h, k, l	I_{hkl}(obs)					
0, 0, 1	207	217 (10)	252 (45)	568 (361)	455 (248)	147 (−60)
1, 0, 0	224	257 (33)	257 (33)	257 (33)	257 (33)	257 (33)
1, 0, 1	110	111 (1)	45 (−65)	111 (1)	45 (−65)	0 (−110)
1, 1, 1	2625	2652 (27)	2492 (−133)	2245 (−380)	2291 (−334)	2938 (313)
0, 0, 2	194	202 (8)	281 (87)	94 (−100)	65 (−129)	337 (143)
2, 0, 0	624	591 (−33)	591 (−33)	591 (−33)	591 (−33)	591 (−33)
1, 0, 2	290	298 (8)	379 (89)	298 (8)	379 (89)	111 (−179)
2, 0, 1 2, 1, 0	216	252 (36)	277 (61)	497 (281)	419 (203)	206 (−10)
1, 1, 2 2, 1, 1	182	199 (17)	91 (−91)	457 (275)	607 (425)	0 (−182)

point suffering a symmetric elongation along c to tetragonal packing in the ferroelectric phase. Pb ions then move along the c-axis by $0.11c=0.46$ A; and Ti ions move in the same direction by $(0.11-0.04)c=0.29$ A.

Our results on $PbTiO_3$ are closest to Evans' *second* model for $BaTiO_3$, in which $\delta z_{OI}=-0.024$ and $\delta z_{OII}=-0.020$. This second model, while not differing significantly from the first model in its value of R, does show a lower quadratic mean error but is ruled out by unreasonable temperature factors. Considering the O-network to be essentially at rest as the structure passes through the Curie point, the second $BaTiO_3$ model would then indicate a shift of Ba by ~0.09 A along c, and a greater shift of Ti in the same direction by ~0.15 A.

It would be unwise to draw conclusions about the tetragonal $BaTiO_3$ structure on the basis of the above results—even though one is tempted to do so. A single-domain-crystal neutron study of $BaTiO_3$ is in progress at the Brookhaven reactor, and results of this will be presented shortly. A final refinement of the $PbTiO_3$ structure is also in progress.

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