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ADSORPTION OF OXYGEN ON THE (110) PLANE OF TUNGSTEN AT LOW TEMP--ETC(U)

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER 5	2. GOVT ACCESSION NO. AD-A090604	3. RECIPIENT'S CATALOG NUMBER 12
4. TITLE (and Subtitle) ADSORPTION OF OXYGEN ON THE (110) PLANE OF TUNGSTEN AT LOW TEMPERATURES.		5. TYPE OF REPORT & PERIOD COVERED (9) Technical
6. AUTHOR(s) 12/ H. Michel, R. Opila and R. Gomer		7. PERFORMING ORG. REPORT NUMBER ONR-N00014-77-C-0018
8. PERFORMING ORGANIZATION NAME AND ADDRESS James Franck Institute University of Chicago Chicago, Illinois 60637		9. CONTRACT OR GRANT NUMBER(s) 15
10. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Physics Program (Code 421) Arlington, Virginia 22217		11. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1425
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 14 TR-E		13. REPORT DATE (11) Oct 1980
		14. NUMBER OF PAGES 23
		15. SECURITY CLASS. (of this report) Unclassified
		16. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of this Report) Approved public release; distribution unlimited		
18. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
19. SUPPLEMENTARY NOTES Preprint-submitted to Surface Science		
20. KEY WORDS (Continue on reverse side if necessary and identify by block number) Adsorption		
21. ABSTRACT (Continue on reverse side if necessary and identify by block number) Isotope labelling experiments have established that the adsorption of O_2 on the W(110) plane at 20 K leads first to the formation of a dissociated atomic layer. A weakly bound molecular species, O_2 , forms only when the atomic layer is essentially complete ($O/W = 0.6$). The desorption of O_2 was found to be first order with an activation energy of $E = 1.9$ Kcal/mole and a frequency factor $\nu = 3 \times 10^{10}$ sec ⁻¹ . The activation energy is shown to be less than the enthalpy of desorption and the meaning of this result is discussed.		

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ABSTRACT

Isotope labelling experiments have established that the adsorption of O_2 on the W(110) plane at 20 K leads first to the formation of a dissociated atomic layer. A weakly bound molecular species, $\alpha-O_2$, forms only when the atomic layer is essentially complete ($O/W = 0.6$). The desorption of $\alpha-O_2$ was found to be first order with an activation energy of $E = 1.9$ Kcal/mole and a frequency factor $\gamma = 3 \times 10^9 \text{ sec}^{-1}$. The activation energy is shown to be less than the enthalpy of desorption and the meaning of this result is discussed.

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In 1976 C. Leung and R. Gomer¹ postulated the existence of a molecular precursor to dissociatively adsorbed oxygen when O_2 was adsorbed at 20 K on the (110) plane of tungsten. The evidence consisted of the following: 1) Work function increased monotonically with exposure, but leveled off at a value much lower than for adsorption above 45 K. 2) On heating to 45 K there was an increase in $\Delta\phi$ together with desorption of part of the layer as O_2 . 3) There was an induction period for the formation of O^+ in electron stimulated desorption from layers kept below 45 K. It was therefore assumed by Leung and Gomer that an initially uniform molecular precursor layer was formed at 20 K, with conversion of part of this layer to atomic O and desorption of the remainder as O_2 when it was heated to 45 K.

Leung and Gomer also found that for sufficiently small exposures the 45 K desorption peak did not show up at all, although $\Delta\phi$ did increase on heating to 45 K. This was interpreted as conversion of the precursor to atomic oxygen without desorption. It was also noted, however, that a weak molecular form, called $\alpha-O_2$ could be readsorbed on the atomic layer and desorbed again at 45 K. Wang and Gomer² confirmed these work function and desorption results and also noted that work function changes on re-adsorption of $\alpha-O_2$ on atomic layers were slightly different from those occurring on heating virgin layers, adsorbed at 20 K. Recently Opila and

and Gomer³ attempted to verify the existence of a molecular precursor by means of UPS and XPS. However no molecular O₂ was seen until the atomic layer was complete, when adsorption was carried out at T ~25 K, the lowest temperature available in the apparatus used. Thus either the interpretation of Leung and Gomer was incorrect, or a very small increase in temperature above 20 K was sufficient to cause atomic rather than molecular precursor adsorption. The present experiments were undertaken in order to settle this point. It turns out that the Leung and Gomer interpretation is incorrect; even at 20 K an atomic layer is first formed, with molecular adsorption occurring only after its completion. However, the $\Delta\phi$ vs. coverage curve of the atomic layer at 20 K differs slightly from that of such a layer formed above, or heated above 45 K. It was also possible to carry out quantitative measurements on the desorption of the molecular α -O₂ species, and these are also reported here.

PRINCIPLE OF THE EXPERIMENT

The idea behind the present experiments is the following. If a uniform molecular precursor layer exists at 20 K, the adsorption history of a given O₂ molecule should not affect its chance of desorbing at 45 K. Specifically if ¹⁸O₂ is adsorbed first, and ¹⁶O₂ is then adsorbed to complete the putative precursor layer, the 45 K O₂ peak should contain both ¹⁸O₂ and ¹⁶O₂ in the ratio in which they occur in the total layer. On the other hand if adsorption first leads to a tightly bound atomic O layer, with a molecular O₂ state forming only on the completed atomic layer, the adsorption history will be important. For the adsorption sequence cited above only ¹⁶O₂ would be seen in the 45 K peak, if ¹⁸O₂ was not adsorbed in excess of the amount needed to form the atomic layer.

This reasoning could be invalidated, in principle, by the following situation: At 20 K two molecular layers form sequentially, the first converting to atomic oxygen on heating without any desorption, the second desorbing without any conversion. This possibility seems rather implausible on physical grounds and is made even more so by the results of Opila and Gomer³ at 25 K.

EXPERIMENTAL

The sequential isotopic dosing experiment was carried out in the apparatus used by Leung and Gomer, described in detail⁴ previously. $^{18}\text{O}_2$ was obtained from Norsk-Hydro and was of 99% purity. Thermal desorption experiments were carried out in the apparatus used by Opila and Gomer,³ which has also been described in detail,⁵ and utilized the cryoshielded source for dosing so that only the front surface of the crystal, facing toward the quadrupole mass spectrometer was covered with oxygen. A temperature controller of new design, shown schematically in Fig. 1 was used in these experiments. This controller also allowed linear ramping of the crystal resistance; over the modest temperature ranges (40-45 K) involved in these experiments, this amounted to linear ramping of the crystal temperature. In essence the controller divides the voltage across the potential leads of the crystal by the heating current and uses the result to drive a programmable power supply which then varies the heating current appropriately. A slightly more detailed description follows. The controller samples the voltage across a stable, high current shunt in series with the crystal and amplifies this signal to obtain V_x . The voltage across the potential leads of the crystal is fed into a differential amplifier whose gain can be accurately varied in known steps. The output from this amplifier, V_z , is divided by V_x in an accurate analogue divider, A5. The resultant output voltage is proportional to the crystal resistance and is

compared with a selectable reference voltage V_r similarly proportional to crystal resistance. The difference voltage is then summed with a voltage proportional to the "resting current" of the power supply, i.e. the approximate current needed to maintain a desired resistance (and hence temperature). The sum is amplified and used as the programming voltage for the power supply. The values of resting current and V_r are determined in equilibrium experiments, i.e. with the crystal resistance not varying with time. By appropriately reducing the frequency response of the amplifiers the controller can then be used to get to preset temperature within 0.5 sec with very little overshoot and to maintain this value with no appreciable drift. In ramped operation V_r is a linear ramp voltage from a digital to analog converter and is stopped at a preset value.

The resistance R vs. T curve of the crystal in the range 20-78°K was obtained from R vs. T values measured in a separate experiment for another (110) oriented single crystal, in the range 20-78°K. In this measurement the crystal was inserted in the He filled cavity of a massive Cu block, and inserted in a cryostat (Fig. 2). A Cu rod extending downward from the Cu block could be immersed in liquid H_2 and heated by a winding of nichrome wire. In this way the temperature in the block could be controlled. Cu-constantan thermocouples, kindly give us by Professor J. W. Stout were inserted in the hollow space of the cell and in the Cu block itself to determine T . The crystal resistance was measured by passing a small current through it and measuring the voltage across it with an accurate microvoltmeter. The curve so obtained agreed closely with the previously used plot of $\log (R - R_0)$ vs. $\log T$, where R_0 is the 4 K, or residual, crystal resistance, which can be obtained from extrapolating the R vs. T curve for a given crystal.

RESULTS

Isotopic Labelling Experiments

Fig. 3 shows desorption spectra as a function of exposure time t at 20 K for the crystal dosed only with $^{18}\text{O}_2$. For $t < 300$ sec there is no 45 K peak at all; for $t = 400$ sec an incipient 45 K peak appears; for $t = 700$ sec this peak has reached its maximum value, and for $t = 800$ sec the first physisorption peak at ca. 27 K comes in. Fig. 4 shows results for initial dosing with $^{18}\text{O}_2$ followed by $^{16}\text{O}_2$ to bring the total dosing time to 700 seconds. For $^{18}\text{O}_2$ doses < 350 sec no $^{18}\text{O}_2$ signal is seen at 45 K. For an $^{18}\text{O}_2$ dose of 400 sec a small $^{18}\text{O}_2$ signal is seen, in agreement with Fig. 3. Also shown is an inverted dosing sequence, 350 sec first of $^{16}\text{O}_2$, followed by 350 sec of $^{18}\text{O}_2$. In this case the 45 K peak is essentially complete as $^{18}\text{O}_2$, and there is also a small $^{18}\text{O}_2$ physisorption peak. Completely analogous results were obtained when $^{16}\text{O}_2$ was adsorbed first and the mass spectrometer set to look for $^{16}\text{O}_2$ in the 45 K peak.

These results show clearly that O_2 desorbing at 45 K does not come from initially adsorbed oxygen but only from that portion of the 20 K layer adsorbed last. More specifically, oxygen adsorbed at coverages too low to give any 45 K desorption does not appear in the 45 K peak. It is known however from the measurements of Wang and Gomer² at 20 K (and confirmed by the measurements of Opila and Gomer³ at 25 K) that the maximum amount of O_2 desorbed at 45 K constitutes 50% of O_2 adsorbable at 20 K (not counting physisorbed oxygen). Thus we may conclude that O_2 appearing in the 45 K peak comes from oxygen adsorbed in the second half of the layer and also that the atomic layer is already saturated when oxygen desorbing at 45 is first adsorbed. O_2 desorbing at 45 K can thus be identified with

α -O₂, a very weakly bound species; it is distinguishable however from physisorbed O₂ by the fact that its maximum amount² is $\sim 4.0 \times 10^{14}$ O₂ molecules/cm². These conclusions cannot be reached quantitatively from the dosing times since the sticking coefficient of O₂ even for a surface temperature of 20 K is less than unity and increases slightly with coverage.⁶

Work Function Measurements

Since the lower work functions of saturated 20 K layers, relative to layers heated above 45 K played a role in leading Leung and Gomer¹ to postulate a precursor, we give here work function results, obtained by the Kelvin method by Wang and Gomer.⁷ Fig. 5 indicates that the differences for 20 K adsorption and 90 K adsorption are very slight at low coverage but become appreciable as saturation of the atomic layer (8.8×10^{14} O atoms/cm²) is reached. Thus there is apparently a slight redistribution, at least of dipoles, when a saturated or nearly saturated atomic layer is heated to >45 K; however the major difference between a layer formed at 20 K and saturated with respect to both atomic and α -O₂ and an atomic layer at >45 K is the decrease in ϕ caused by α -O₂. These conclusions are also consistent with the heating data of a saturated 20 K layer shown in Fig. 7 of Ref. 2.

It was also attempted to measure $\Delta\phi$ vs. coverage at 25 K by using a Leed gun and retardation in the apparatus of Opila and Gomer. These measurements, although not very accurate showed very similar trends. Interestingly enough at low coverage the retardation results at 25 K showed the small negative work function increment reported by Bauer et al.⁸ We have no explanation for this result.

Desorption Measurements

Alpha-layers were prepared by adsorbing a saturated layer at 25 K, heating to 90 K and readsorbing alpha-O₂. Fig. 6 shows simultaneous traces of temperature and desorption signal in the mass spectrometer vs. time for desorption from a full alpha-layer at 42 K. Fig. 7 shows a representative plot of the logarithm of mass spectrometer signal (proportional to desorption rate) vs. time. These plots are linear, indicating that the desorption is first order. Fig. 8 shows a plot of $\ln k$ vs. $1/T$, k being the rate constant obtained from the slope of graphs like those of Fig. 7.

The values of prefactor and activation energy obtained from these results are $\gamma = 3 \times 10^9 \text{ sec}^{-1}$ and $E = 1.9 \text{ Kcal/mole}$. Also shown are points obtained by the same procedure for direct adsorption to saturated atomic plus alpha-O₂ layers at 25 K. Although there is somewhat more scatter in these results they yield almost the same value of E , $= 1.9 \text{ Kcal/mole}$ and $\gamma = 1 \times 10^{10} \text{ sec}^{-1}$.

Temperature programmed desorption was also carried out by increasing the resistance and thus the temperature of the crystal linearly with time. The experiments were carried out with the same heating rates for various initial coverages, as indicated in Fig. 9. The results were analyzed as follows: The ordinate $y(R)$ of any plot in Fig. 9 for a given R and hence T is proportional to the desorption rate at that point:

$$y(R) = c_1 \dot{O}_2 \quad (1)$$

where c_1 is a constant. The integral under a given curve from R to ∞ is proportional to the α -O₂ coverage remaining on the surface at that point:

$$O_2 = (c_2 / c_1) \int_R^\infty y(R) dR = (c_1 / c_2) A \quad (2)$$

where A stands for the integral and

$$c_2 = (dR/dt)^{-1} \quad (3)$$

Thus plots of y vs. A should be linear for first order kinetics since

$$\dot{O}_2 = k O_2$$

or using Eqs. (1) and (2)

$$y = k c_2 A \quad (4)$$

Fig. 10 shows plots of desorption rate vs. A. The plots are linear but do not pass through the point (0,0), almost certainly because of spurious "tails" on the high temperature side of the desorption curves resulting from slight anisotropies of crystal temperature and desorption from the ends of the support rods. Nevertheless plots of $\ln k$ vs. $1/T$ obtained by using the slopes of the curves, yield a good straight line (Fig. 11) and values of $\nu = 10^{10} \text{ sec}^{-1}$, $E = 2.0 \text{ Kcal/mole}$.

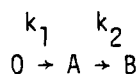
DISCUSSION

Nature of the Low Temperature Layer

The present results indicate that the initial layer formed is atomic oxygen; when this layer is almost or completely saturated a molecular state, $\alpha\text{-O}_2$ can be adsorbed. This state desorbs around 45 K and its amount is fixed. As previously found by Wang and Gomer², and confirmed by Opila and Gomer³ the total amount of oxygen (measured as atoms) that can be held as $\alpha\text{-O}_2$ is equal to that held as atomic oxygen, i.e. there are 0.5 molecules of $\alpha\text{-O}_2$ per O atom in the chemisorbed layer at $O/W = 0.6$. For completeness it should also be mentioned that physisorbed O_2 can be adsorbed once the α -layer is complete, as found previously^{1, 2}. This desorbs around 25-27 K.

The 20 K atomic layer seems to differ slightly from the $T > 45$ K form in that the dipole moment per atom seems slightly smaller. This could result from a slight rearrangement on heating.

The desorption kinetics of α -O₂ reveal an interesting feature. From the fact that α -O₂ desorbs at almost twice the desorption temperature of physisorbed O₂ it is safe to conclude that its binding energy must exceed that of physisorbed O₂. The binding energy of the latter, however, must exceed the sublimation energy of O₂ or it would be unstable with respect to the latter. In any case it cannot be less than the sublimation energy, which is 1.9 Kcal/mole. Thus the binding energy of α -O₂ must be appreciably greater than 1.9 Kcal/mole. Consequently, the activation energy of α -O₂ desorption is less than its binding enthalpy. We have recently obtained analogous results for thermal desorption of Xe from the (110) plane of W.⁹ These results are in qualitative agreement with recent theoretical work by Freed and coworkers.¹⁰ Most simply put, for weak binding and sufficiently anharmonic potential curves, there exists a critical vibrational energy level, from which an adsorbate atom will be excited all the way to desorption by lattice phonons with much higher probability than that of losing energy and returning to the ground state. Put in somewhat simplified terms one may consider the desorption as a 2 step process: excitation from the ground state 0 to the critical level, A followed by desorption to B: If the backward processes can be neglected the scheme is then



and if $k_2 \gg k_1$ the rate will be controlled by k_1 with an activation energy corresponding to the energy difference between 0 and A, which is clearly

less or equal to the enthalpy of desorption, which given by the energy difference between O and B. This scheme does not violate thermodynamics since at equilibrium the inverse processes cannot be neglected and the equilibrium amounts of O, A, and B will all be correctly described by thermodynamic factors in the usual way.

The present results indicate that it is not always possible to equate kinetically derived activation energies of desorption with corresponding enthalpies, even in the absence of an activation energy of adsorption. Most probably the differences are most important for weak binding.

ACKNOWLEDGMENT

This work was supported in part by ONR Contract N00014-C-0018. We have also benefited from the Materials Research Laboratory of the National Science Foundation at the University of Chicago.

FIGURE CAPTIONS

- 1) Schematic block diagram of temperature controller described in text.
- 2) Schematic diagram of apparatus used for determining R vs. T curve of crystals in range 20-80K.
- 3) Thermal desorption spectra of α -O₂ for different dosing times (indicated by numbers in Figure) for ¹⁸O₂ adsorbed at 20 K. The data were obtained by increasing the crystal resistance almost linearly with time. The temperature values shown are approximate.
- 4) Thermal desorption of ¹⁸O₂ for adsorption sequences indicated on figure. The numbers and the order in which they appear stand for dosing times and sequences: e.g. 200 ¹⁸O₂ + 500 ¹⁶O₂ stands for 200 sec dose of ¹⁸O₂ followed by a 500 sec dose of ¹⁶O₂.
- 5) Work function increment $\Delta\phi$ vs. coverage for dosing at 20 K and for heating to 90 K after dosing. The 20 K curve is from unpublished results of Wang and Gomer, the 90 K curve from Ref. 2.
- 6) Simultaneous graphs of crystal temperature and desorption rate for α -O₂ desorption at 42 K.
- 7) Plot of the logarithm of the mass spectrometer signal (proportional to desorption rate) vs. time, for isothermal desorption.
- 8) $\ln k$ vs. $1/T$ for isothermal desorption of α -O₂. Data for α -layers prepared on a O/W layer heated to 100 K and on a freshly covered layer prepared at 25 K (virgin layer) are shown.
- 9) Thermal desorption spectra for various initial coverages of α -O₂ on a saturated O/W layer. Time, crystal resistance and temperature are shown.
- 10) Plots of mass spectrometer signal (proportional to desorption rate) vs. area remaining under the curves of Fig. 9 (proportional to coverage) for temperature programmed desorption.
- 11) Plots of $\ln k$ vs. $1/T$ obtained from the data of Fig. 10.

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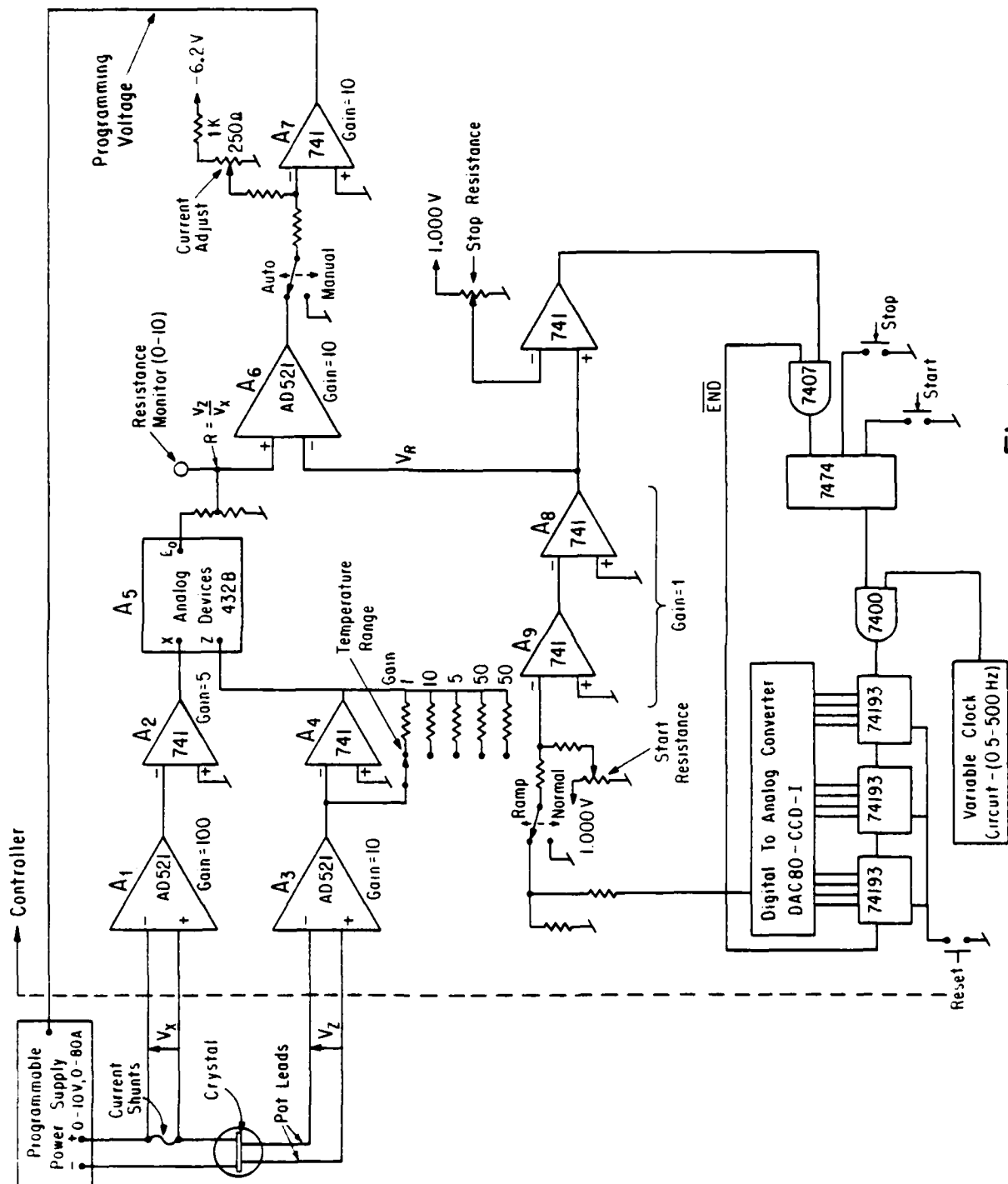


Fig.1

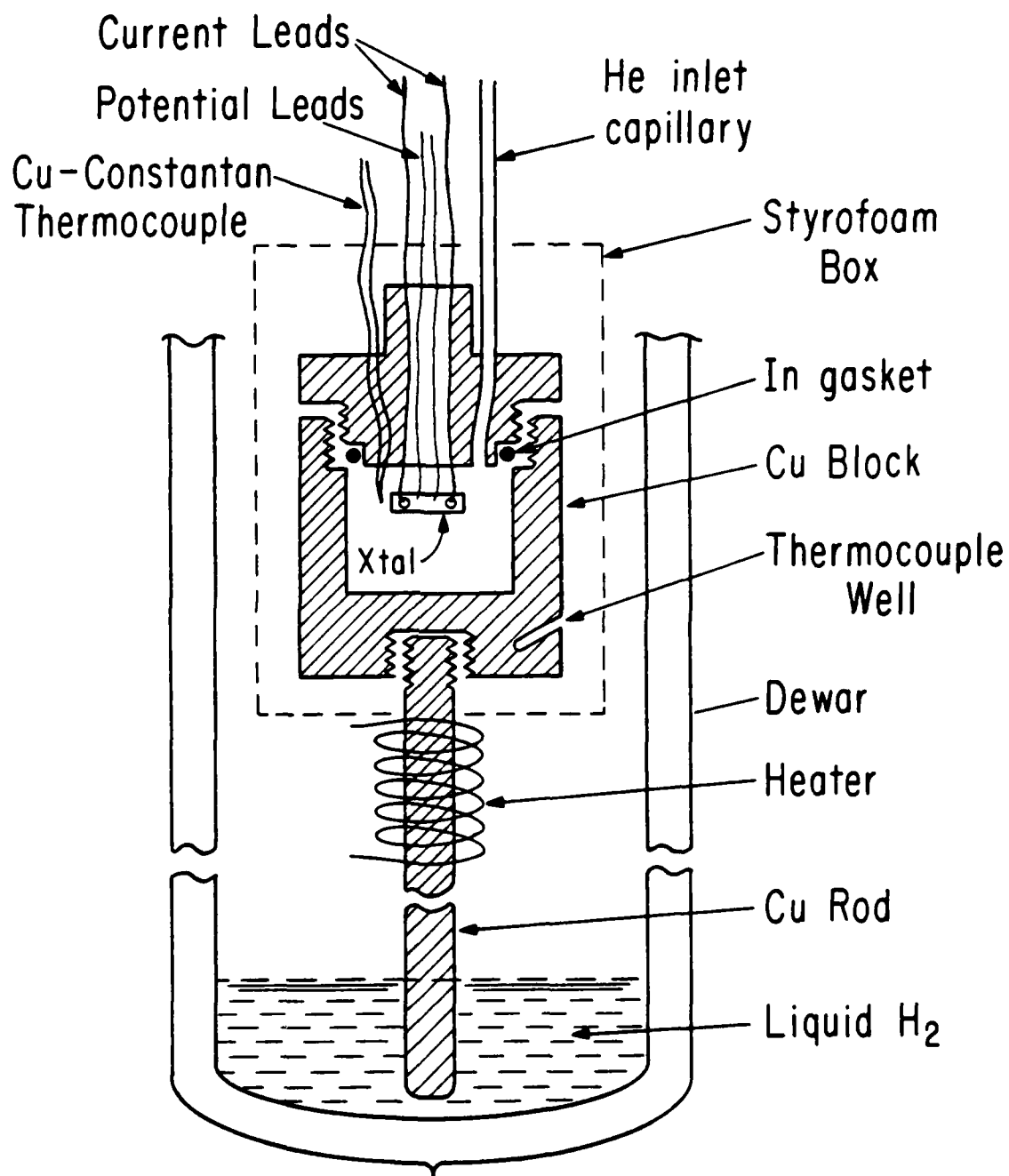


Fig.2

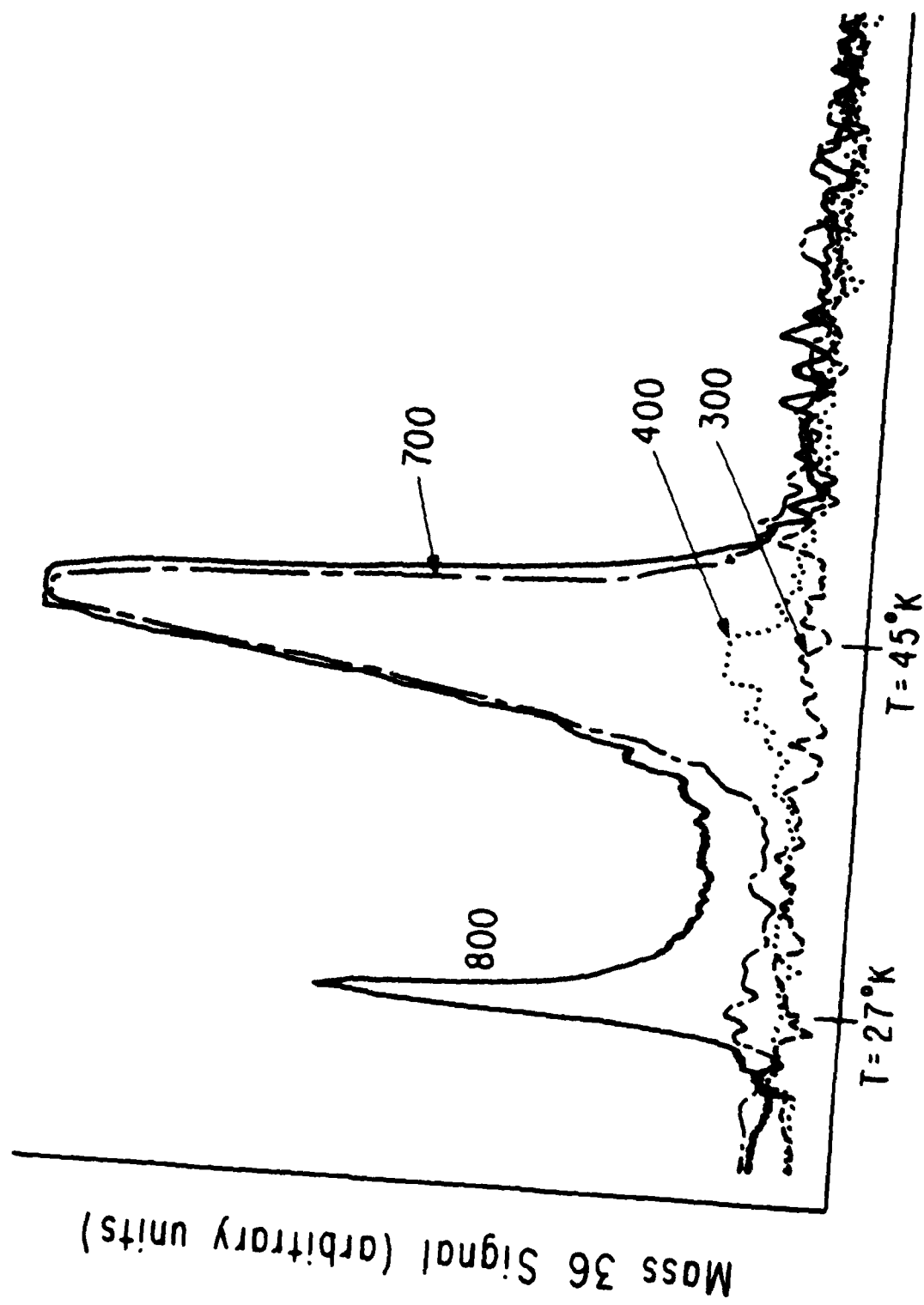


Fig. 3

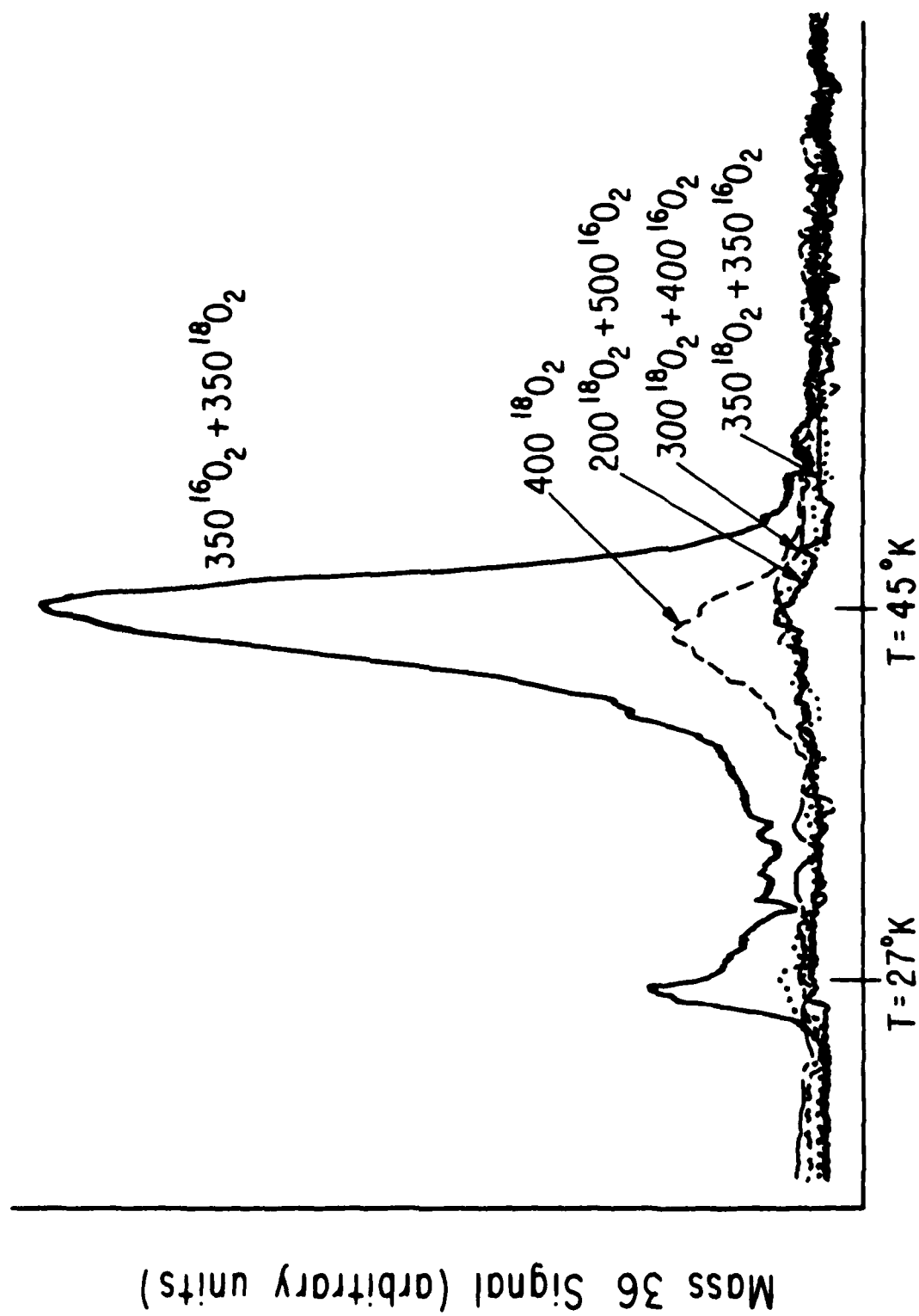


Fig. 4

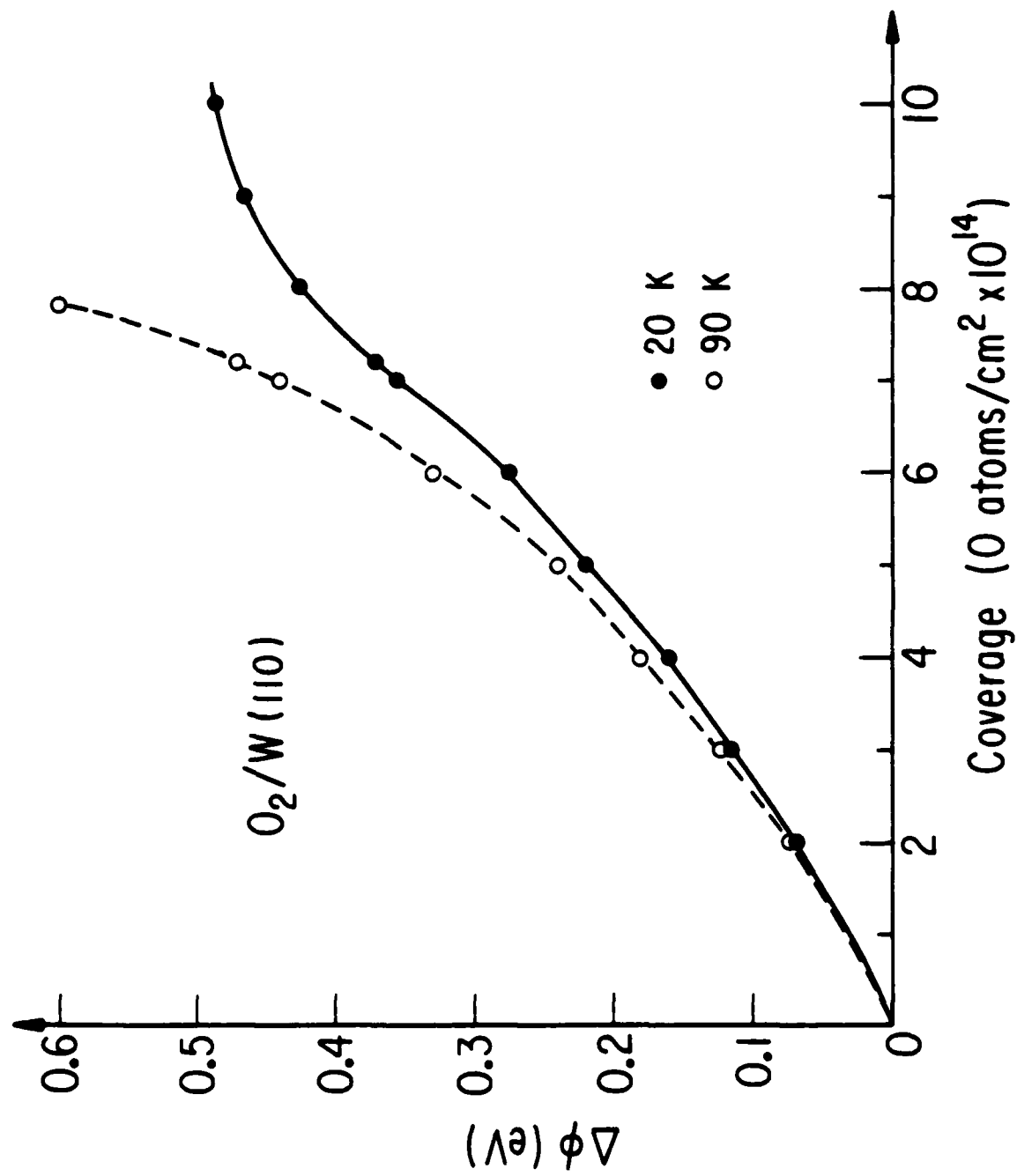


Fig.5

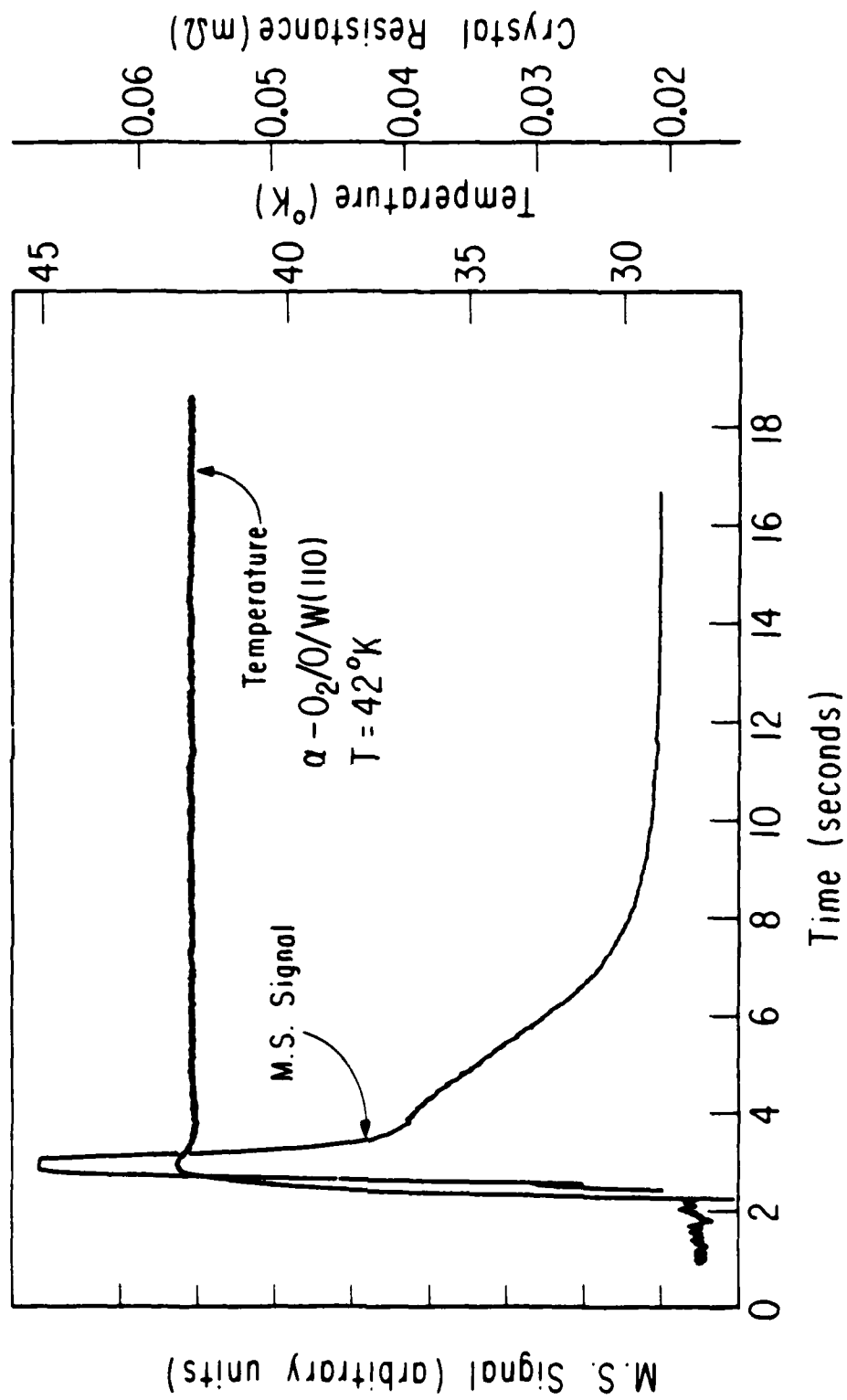


Fig.6

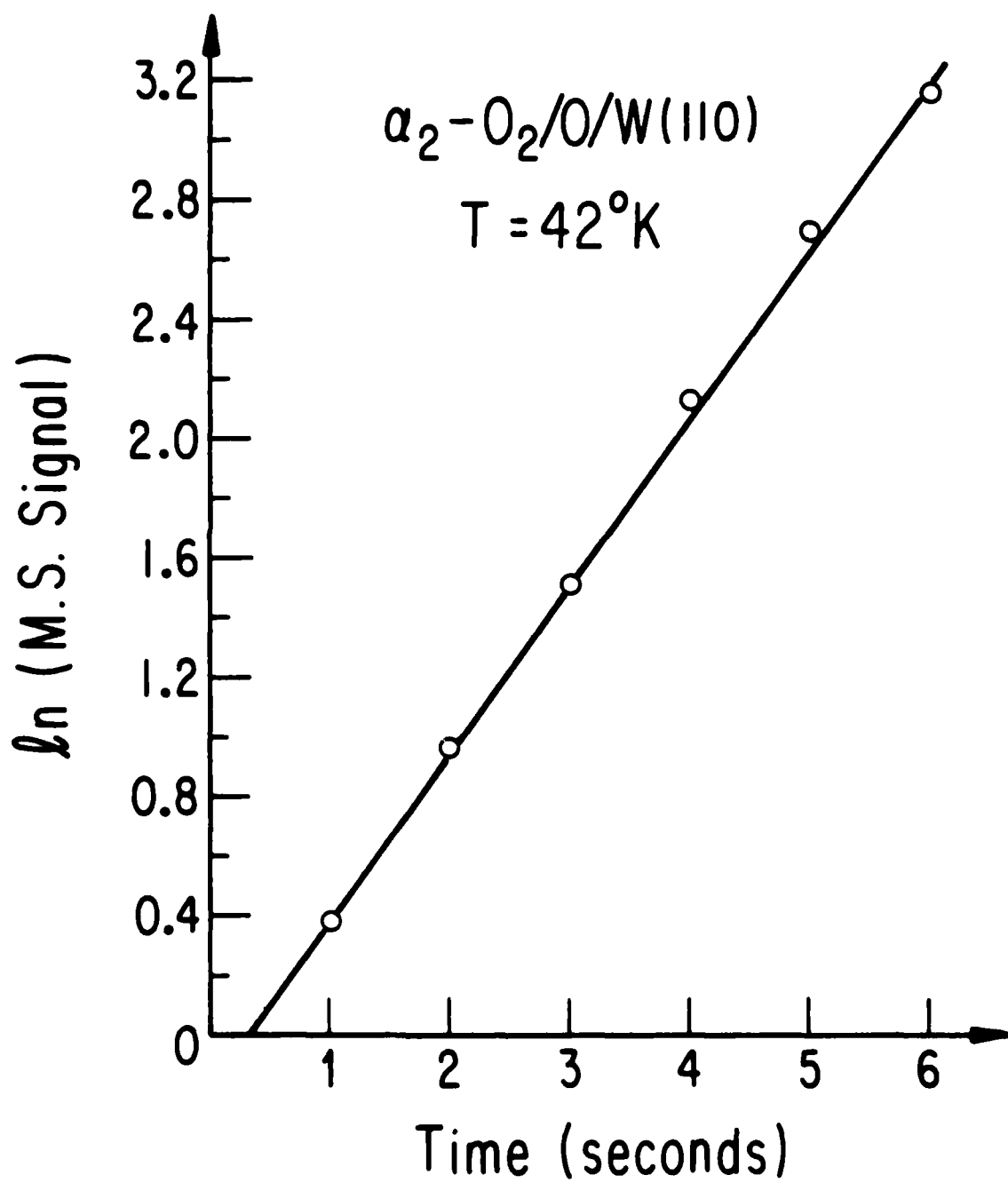


Fig.7

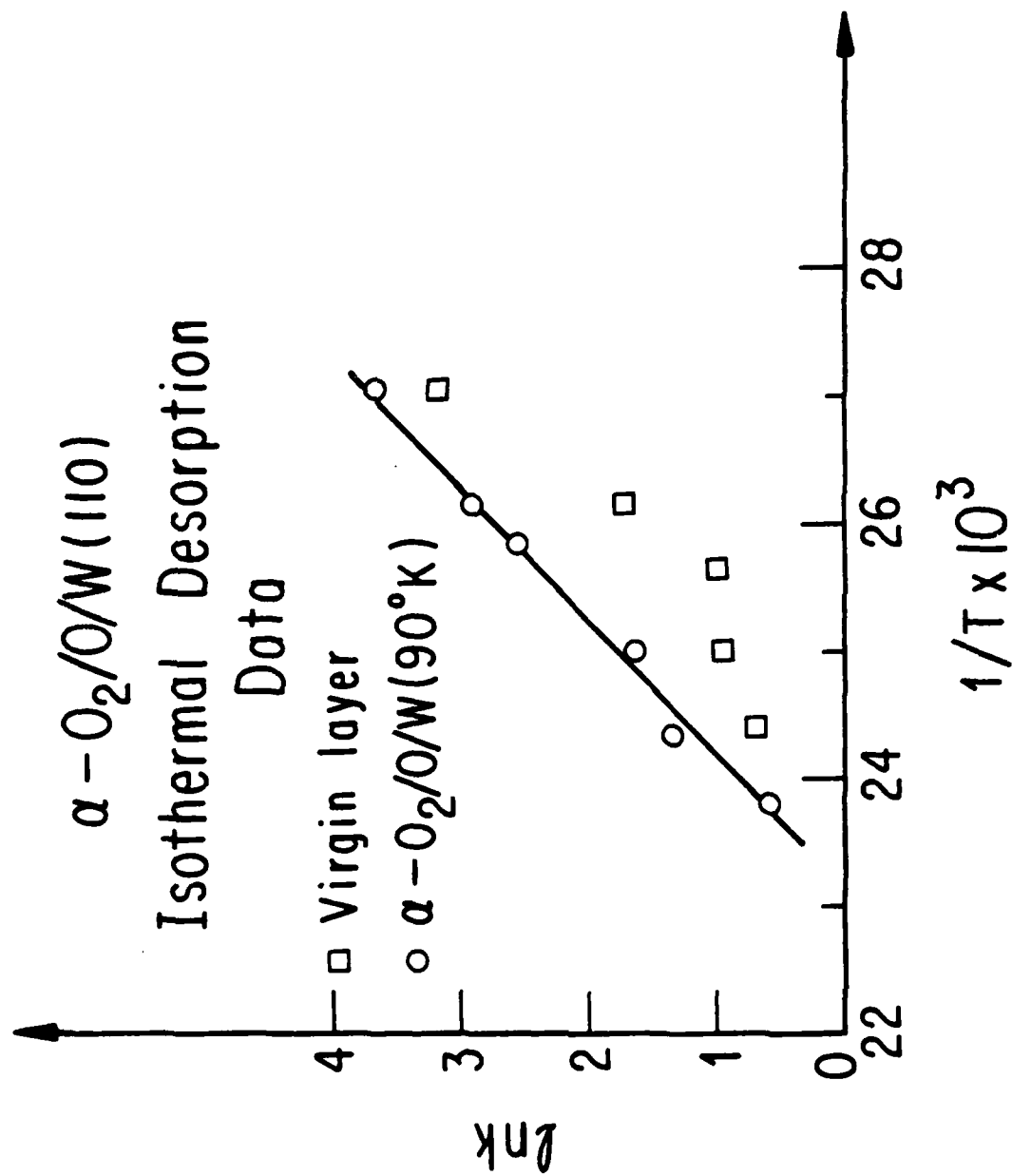


Fig.8

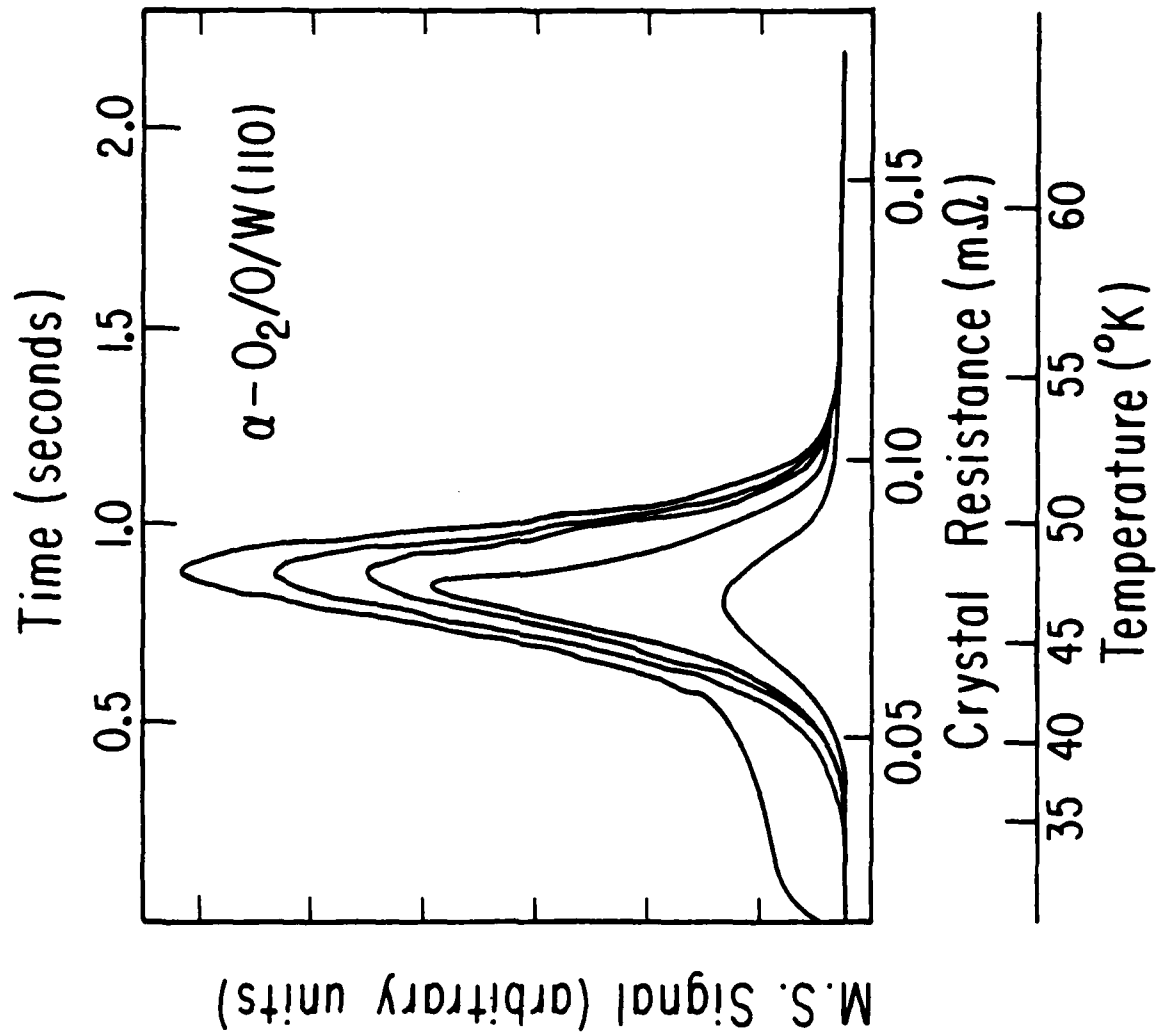


Fig. 9

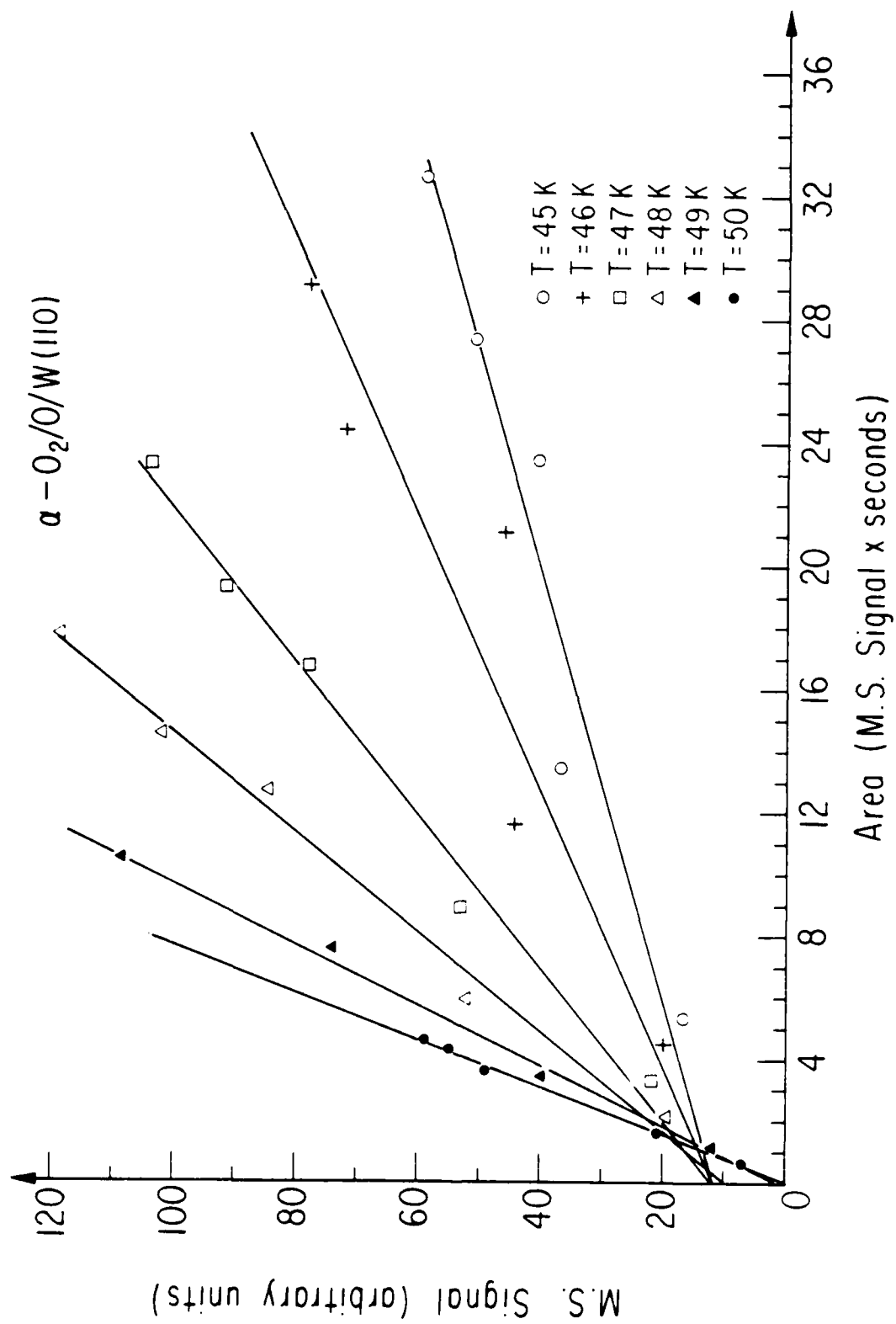


Fig.10

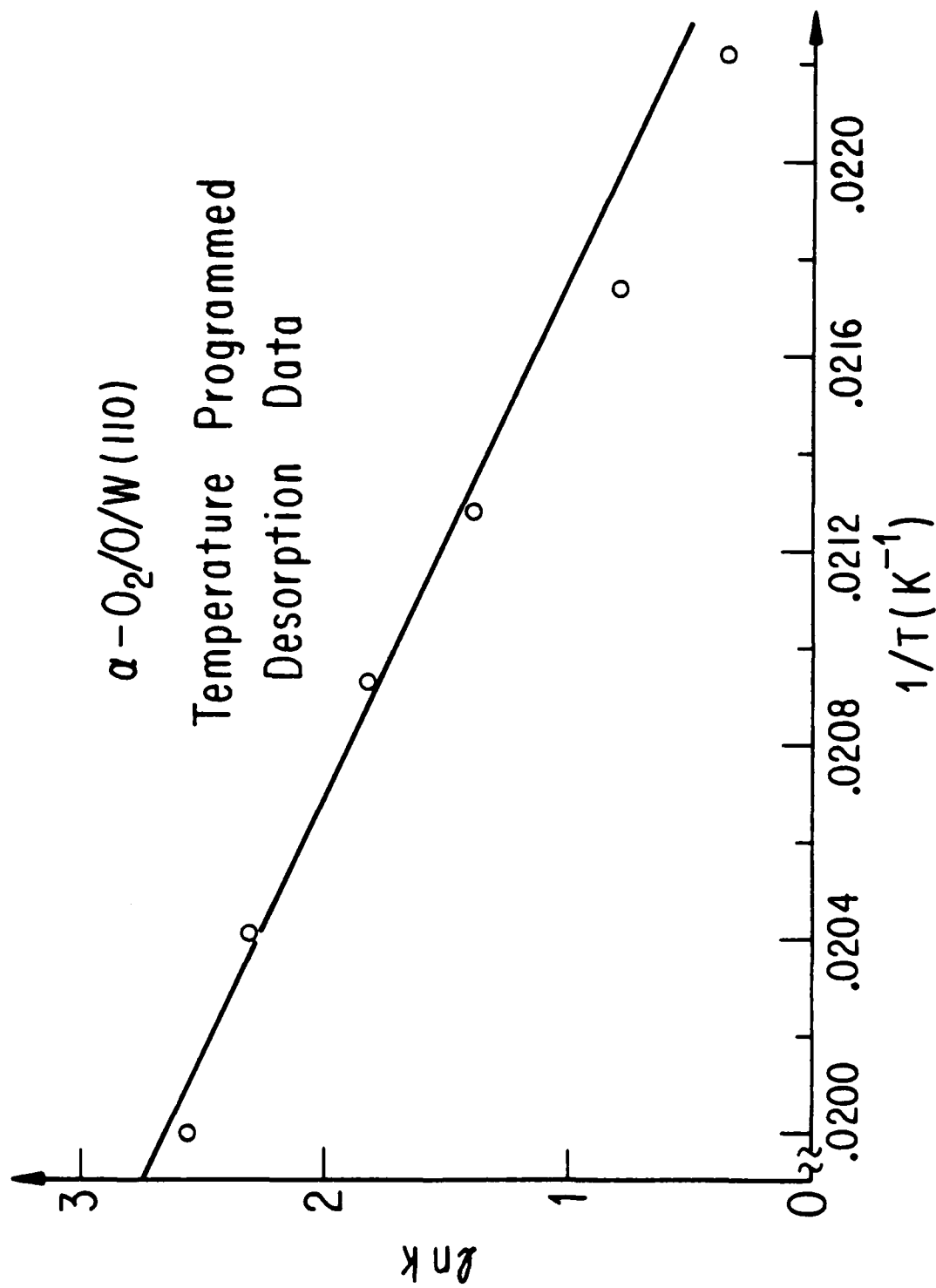


Fig.11

