It seems therefore possible that in some way the presence of $5d$ and $4f$ bands of the substituted rare-earth ion and the magnetism of the latter may play a role in the first-order phase transition discussed in this paper. Further detailed studies are in progress and the results will be published elsewhere.

We are much indebted to Dr. W. M. Walsh, Jr., Dr. T. M. Rice, and Dr. W. F. Brinkman for very helpful discussions. We wish to thank Mrs. A. S. Cooper for lattice-parameter measurements and Mr. R. G. Maines for assistance.

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[2]These transition temperatures were arbitrarily taken as the midpoints in the temperature intervals over which this phase change occurred for each sample. We believe that the existence of a temperature interval is mainly due to residual strain introduced during grinding and the extreme sensitivity of the transition temperature to strain. It is also possible that there is a narrow composition gradient which will contribute to this.

[3]The designations B, B', and M for the phases signify respectively the normal black phase, the black phase stable at low temperature with lattice parameter $a = 5.82$ Å, and the golden-colored metallic phase.

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[8]The lattice parameter of the M phase is independent of T between 225°K and the transition temperature ($M \rightarrow B'$), signifying that with cooling there might actually be a slight expansion in volume counteracting the normal contraction. This would support the contention that the $4f$ band lowers with decreasing T and becomes fractionally occupied.

[9]The lattice parameters of $Sm_{0.84}Gd_{0.16}S$ and $Sm_{0.78}Gd_{0.22}S$ are 5.68 and 5.66 Å, respectively. The lower lattice parameter for the latter is equivalent to greater positive pressure and hence higher compressional energy. Therefore, we are justified in assuming that the higher the Gd concentration the greater would be the elastic energy needed for expansion.

[10]There is a weak pattern in the x-ray powder photographs from Y_2O_2S. Because of this, the actual Y concentration in $Sm_{1-x}Y_xS$ may be lower than the amount of Y added.

Measurement of Lifetimes and Binding Energies of Atoms Adsorbed on Surfaces at Low Temperatures by a Rapid-Flash-Desorption Technique*

S. A. Cohen† and J. G. King

Department of Physics and Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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A dynamic method for measuring the characteristic lifetimes and binding energies of physisorbed atoms is described and results presented. We find for ~1.5 monolayers of helium adsorbed on Constantan an isosteric binding energy of 31± 1°K and a characteristic lifetime of $(2\pm 0.5)\times 10^{-7}$ sec. The velocity distribution of the desorbing atoms is found to be non-Maxwellian.

By means of low-temperature atomic beam techniques we have performed rapid-flash-desorption experiments in which $\Delta T/\Delta t$ is greater than 10^7 °K/sec; complete desorption occurs in times as short as 10^{-8} sec. For ~0.5 monolayers of helium adsorbed on top of ~1.0 monolayers of helium previously adsorbed on Constantan we find a binding energy E of 31 ± 1°K/atom, equal to that simultaneously measured[1] by adsorption isosteres; and a characteristic lifetime τ_0, for $4°K < T < 18°K$, of $(2\pm 0.5)\times 10^{-7}$ sec, 6 orders of magnitude longer than the Frenkel[2] value, but consistent with the trend shown in recent quantum-mechanical calculations by Bendow and Ying.[3] Nondimensional similarity parameters for this system fall near the $n = 4$ resonance in the theory of Pagni and Keck,[4] which offers a classical explanation for long lifetimes. The observed velocity distribution differs from that of atoms effusing in a beam from a Maxwellian source by a factor of v^{-1}. This method has the advantage over isotherm,[5] isostere,[6] and quasi-steady-state[7] measurements in that in addition to the binding energy it gives the desorption velocity distribution and the characteristic lifetime τ_0 independently of the sticking coefficient and uncomplicated by desorption caused by gas bombardment or stray infrared radiation.[8] Besides being a contribution to the rapidly growing field of surface physics, these results have bearing

on the understanding of molecule formation on interstellar dust grains.[9]

The apparatus operates in a liquid-helium bath and is a vacuum vessel containing a field-ionization detector pointing at the first dynode of an electron multiplier. Two Constantan wires, nominally 2.54×10^{-3} cm in diameter and 1.4 cm long, are mounted on a superfluid-filled U-shaped oxygen-free high-conductivity copper block with their centers 2.07 and 3.66 cm below the detector. One side of each wire is grounded to the copper block; the other is attached by pressed indium contacts to an Al_2O_3 wafer cemented to the copper block with Apiezon *N*. Trapezoidal pulses of 100 V maximum height and 50 nsec minimum duration can be applied through coaxial cables to heat either wire. The impedances of the wires are matched to the cables and the voltage pulser. Each wire's diameter was measured interferometrically to 0.5% accuracy at six different points. Enthalpy values were taken from data compiled by Keesom and Kurrelmeyer[10] for Constantan of equal Ni-Cu percentages prepared by the same manufacturer.[11] The base temperature of the wires (always below the λ point) was assumed to be the same as the temperature of the copper block, which was determined by the usual methods. The temperature rise of the Constantan wire caused by a single voltage pulse can be calculated from these data to $\pm 3\%$. The maximum temperature rise was 25°K. The cool-down time constant of the wire, evaluated from data on the rate of vapor deposition after a heat pulse, was 0.1 sec, consistent with the calculated value. The measured vapor deposition rate, determined from a plot of the number of detected atoms versus time between heat pulses, was usually in the range of 1–10 sec for 95% replenishment. This yields the sticking coefficient, which equals 0.4 ± 0.2 on the bare Constantan surface.

In a typical experimental run a Constantan wire was pulsed once every 20 sec for 8 h. Those desorbed atoms that reached the detector were ionized and accelerated to the first dynode of the electron multiplier. The multiplier output was amplifed and stored in a multichannel scaler with 10-μsec bins. Figure 1 shows results from a set of runs in which the calculated peak temperature of the 2.07-cm distant wire ranged from 4 to 18°K and the duration of each heating pulse was approximately 5×10^{-8} sec. The peak of the arrival-time distributions (t_p) is plotted against $T^{-1/2}$. For T between 8 and 18°K, t_p is linear

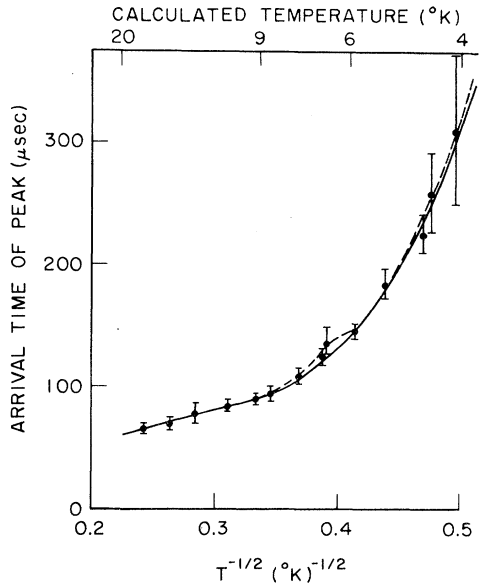

FIG. 1. Observed and calculated times of the peak of the arrival-time distribution of helium desorbed from Constantan by a rapid (50 nsec) heating versus $T^{-1/2}$. Solid curve, computed based on the model that there is one type of adsorption site where the binding energy is 31°K and the characteristic adsorption lifetime is 2×10^{-7} sec. The detector sensitivity is proportional to v^{-1}. The desorbed-atom velocity distribution is $v^{-1}\times$(Maxwellian). Dashed curve, modeled by three types of sites with binding energies 31, 50, and 90 °K/atom; characteristic lifetimes 2×10^{-7}, 1.5×10^{-7}, and 1.2×10^{-7} sec, in the population ratio 3:4:1. The detector sensitivity and velocity distribution are the same as for the one-state model.

with $T^{-1/2}$; and for T between 4 and 8°K, t_p diverges toward later times. The slope of the linear region is $t_p = 0.835\pm0.025\,t_0$, where $t_0 = L/v_0$, $v_0 = (2kT/M)^{1/2}$, and L is the geometrically weighted distance from the wire to the detector, $\simeq 2.12$ cm. The integral-power, Maxwell-like function which most closely fits the observations is given by

$$dn(t) = (t_0^2/t^3)\exp(-t_0^2/t^2)\,dt, \qquad (1)$$

which peaks at $t = 0.816t_0$. In contrast, the arrival-time distribution of a short burst of atoms effusing from a Maxwellian source is given by

$$dn_M(t) = (t_0^4/t^5)\exp(-t_0^2/t^2)\,dt, \qquad (2)$$

which peaks at $t = 0.633t_0$. Of the two missing factors of t one can be accounted for by the v^{-1} sensitivity of the field-ionization detector.[12,13] The other is attributed to the velocity distribution of the desorbing atoms. Other runs with the detector to wire separation varying up to 3.66 cm gave the same results over this temperature range.

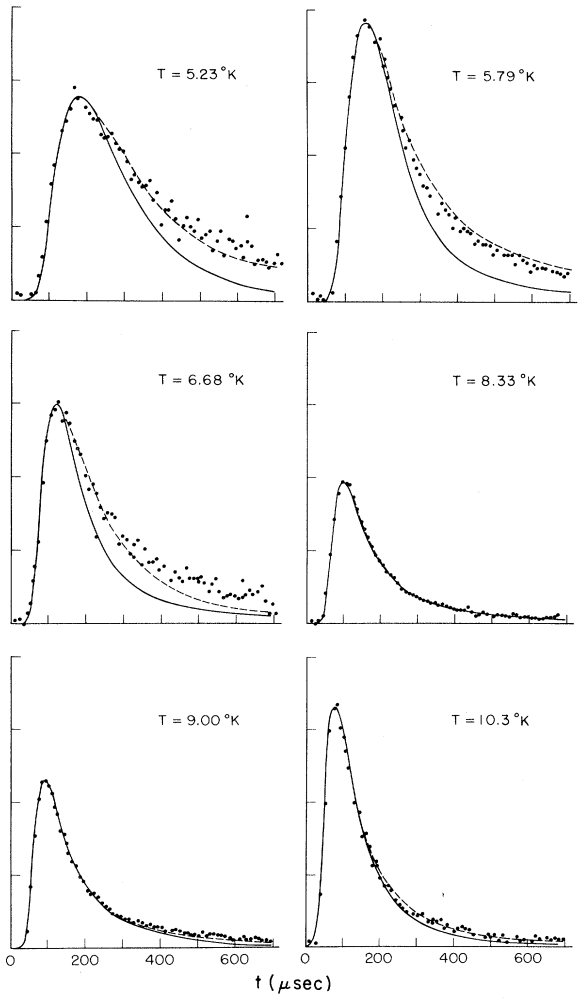

FIG. 2. Observed arrival-time distributions: the relative number of atoms that reached the detector per 10-μsec interval after the heating pulse ($t=0$) for six different wire temperatures. The detector was 2.07 cm above the center of the wire. Also plotted are computed arrival-time distributions based on the model, lifetime on the surface $=\tau_0\exp(E/T)$, and the convolution of the desorbed atom velocity distribution with the detector velocity-dependent sensitivity proportional to $v^{-2}\times$(Maxwellian). The computer curves are normalized to the data at the peak. The six curves are not normalized with respect to each other. Circles, data; solid lines, one-state system, $\tau_0=2\times10^{-7}$ sec, $E=31$ °K/atom; dashed lines, three-state system, $\tau_0=2\times10^{-7}$, 1.5×10^{-7}, 1.2×10^{-7} sec, $E=31$, 50, and 90 °K/atom; the initial numbers of adatoms in each state are in the ratio 3:4:1.

Individual arrival-time distributions for $8<T<18$°K, some of which are shown in Fig. 2, were subjected to a mean-square fit by Eq. (1) for $0.5t_p\leq t\leq 1.5t_p$. This redefined the previously estimated arrival of the peak and also set the criteria for the error bars. The error bars are 90% probability on the t test of significance. Under the assumption that the lifetime of atoms on the surface is given by $\tau=\tau_0\exp(E/T)$ and that the velocity distribution of the desorbed atoms is the efflux Maxwellian multiplied by v^{-1}, theoretical arrival-time distributions were generated by computer for $\tau_0=10^{-7}$, 10^{-9}, and 10^{-11} sec, and for binding energies ranging from 20 to 100°K (Fig. 3). These curves show the sensitivity of the method to E and τ_0. The best fit for the data presented in Fig. 1 is obtained with $E=31$°K and $\tau_0=2\times10^{-7}$ sec.

Comparison of the individual computer-generated arrival-time distributions (Fig. 3) with the experimental ones reveals an excess of late-arriving atoms in the experimental data. By placing a 1.6-cm$\times$0.1-cm movable shutter parallel to the Constantan wire, midway between it and the detector, it was determined that this excess was not due to rebounding atoms. The signal with the shutter in place occurred at $200<t<600$ μsec and was (1.4 ± 0.4)% of the total signal with the shutter displaced. By including more tightly bound atoms known to exist by previous isostere measurements[1,6] in the calculated arrival-time distribution through a "three-state adsorption" model, it was possible to improve the fit of the individual arrival-time distributions found in Fig. 2 without greatly affecting the arrival times of the peak (Fig. 1). The values for the energies (E_1,E_2) used for the two additional states were chosen from considerations of isostere data. The characteristic lifetimes chosen were shorter than 2×10^{-7} sec by the factor $(31\text{°K}/E_{1,2})^{1/2}$. Further runs at approximately 0.15 monolayer coverage showed the higher binding energy directly in the curve of arrival time of the peak versus $T^{-1/2}$. Because of decreased signal the error is much larger: $E=65\pm15$°K/atom, $\tau_0=10^{-7\pm1}$ sec. The relative number of detected atoms versus the temperature is consistent with the predictions of the three-state model.

In another series of runs with 10^{-7}-sec-duration heating pulses and with peak temperatures up to 25°K the data show identical results for $4<T<20$°K. Near 25°K, however, the observed arrival-time distributions were "slow." This implies that the adsorbed atoms desorb in a time shorter than, or comparable to, the length of the heating pulse—before the surface has reached maximum temperature. With $E=31$°K we obtain $\tau_0(25\text{°K})=4\times10^{-8}$ sec from the data. Thus τ_0 is not independent of T. Experiments performed over the same temperature range with H_2 ad-

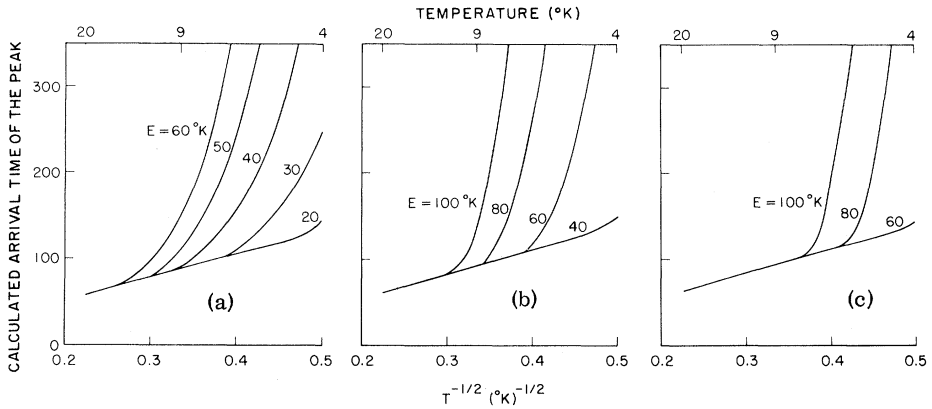

FIG. 3. Calculated time of the peak of the arrival-time distributions versus (temperature)$^{-1/2}$ for different values of characteristic lifetime τ_0 and binding energy E. (a) $\tau_0 = 10^{-7}$ sec; $E = 20$, 30, 40, 50, 60°K. (b) $\tau_0 = 10^{-9}$ sec; $E = 40$, 60, 80, 100°K. (c) $\tau_0 = 10^{-11}$ sec; $E = 60$, 80, 100°K. These curves assume instantaneous heating of the surface on which helium atoms are adsorbed. The surface is 2.12 cm from the detector; the atoms desorb with v^{-1} $\times$ (Maxwellian); the detector has a v^{-1} sensitivity.

sorbed on Constantan also yield long lifetimes, of order 10^{-7} sec.

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†Present address: Princeton Plasma Physics Laboratory, Princeton University, Princeton, N.J. 08540.

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