Table 1. Materials used in preparing superconducting ZrB_{12} samples. Boron lots are listed in their order of appearance (left to right) in Fig. 1.

Material	Isotopic comp. (av. atomic mass)	Chemical purity (%)*	Impurities (ppm)†			No. of samples
B^{10}						
Lot 1	10.04	97.6	Ca, 1000 K, 100 Ni, <500 C, 7500	Cu, 500 Mg, 200 Si, 5000	Fe, 1000 Mn, <200 Ta, 500	2
B^{10}						
Lot 2	10.04	99.97	Si, 200 Ca, 4	Mg, 5	Fe, 53	2
Natural B						
Lot 1	10.81	99.75	C, 1100	Fe, 1400		4
Lot 2	10.81	99.9995				3
B^{11}	10.98	99.89	Si, 1100	Mg, 4		5
Zr	91.22	99.2	C, 175 Hf, 190 O, 980 Ti, 70	Cr, 150 N, 119 Ta, <200	H, 125 Nb, <100 Si, 75	

* By weight. † Oxygen content in boron lots unknown.

and if we give greater consideration to samples which neither shattered nor exhibited "tails." We may then express the isotope effect as $T_c \propto M^\alpha$, $\alpha = -0.09 \pm 0.05$, where M is the boron mass, assuming the usual exponential dependence of T_c upon M. A value of $\alpha = -0.16 \pm 0.09$ is obtained if the total mass is used.

These values of α would seem to demonstrate that the superconductivity of the compound ZrB_{12} is not readily identifiable with that due to a hypothetical metallic boron. It is apparent, however, that phonon modes involving boron atoms are pertinent. Further interpretation is difficult for several reasons, particularly the fact that any zirconium contribution to the superconductivity of ZrB_{12} would be likely to strongly influence the boron isotope effect, since elemental zirconium itself shows a vanishing isotope effect (*6*). Little detailed theoretical work has been done on the significance of isotope effects measured in compounds, and few, if any, isotope effects have been determined in systems analogous to ZrB_{12}. Engelhardt *et al.* (*7*) found the boron isotope effect in W_2B to be $\alpha = -0.090 \pm 0.016$, using the boron mass only for calculation, but in Mo_2B the same measurement gives (*7*) $\alpha = -0.004 \pm 0.016$, making the results difficult to interpret in relation to elemental boron. If the molybdenum mass alone is used for calculation, the molybdenum isotope effect in Mo_2B ($\alpha = -0.42 \pm 0.02$) (*7*) is approximately the same as in the element ($\alpha = -0.37 \pm 0.04$) (*8, 9*). In $MoBe_{22}$, which has cubic symmetry and may be more analogous to ZrB_{12} (*1*), the molybdenum isotope effect is changed to $\alpha = -0.23 \pm 0.10$ (*8*). This is close to the value for molybdenum in Mo_3Ir (*9*) ($\alpha = -0.20$), again if the molybdenum mass alone is used for calculation. On this basis, the transition-metal character of the superconductivity of molybdenum is retained completely in Mo_2B, where the boron isotope effect vanishes, and is as evident in $MoBe_{22}$ as in Mo_3Ir.

Perhaps a clear-cut demonstration of any tendency of a hypothetical cubic boron [or cubic beryllium (*1*)] toward superconductivity can only be accomplished in the absence of transition elements, which have always been essential so far for the superconductivity of boron (and beryllium) compounds (*1, 5, 8, 10*). The hexa- and dodecaborides formed with the rare earths produce only magnetic compounds (*1, 11*).

Aluminum and gallium, which are in the same column in the periodic table as boron, form high T_c compounds with niobium isomorphous with Nb_3Sn (*5*) ($T_c = 18°K$). In Nb_3Sn, the tin isotope effect is very small (*12*) ($\alpha = -0.02$, -0.08, depending on the mass used for calculation), although tin in its elemental form exhibits a normal isotope effect ($\alpha = -0.5$) (*13*). Thus the superconductivity of the compound is not characteristic of the nontransition metal. It would seem that, under favorable conditions, nontransition elements in compounds with transition elements either enhance the *sd*-interactions responsible for superconductivity in the transition metals, which show reduced isotope effects, or introduce phonon modes conducive to high T_c's for which the effect of isotopic mass has not been studied.

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Venera 4 Probes Atmosphere of Venus

Abstract. *The atmospheric data and information on trajectory received from Venera 4 together provide consistent and firm evidence of its success in reaching the surface of Venus.*

On 18 October 1967 a Russian probe entered the atmosphere of Venus and transmitted the first measurements ever made *in situ* of the atmosphere of a planet other than Earth. When the complete results of this major accomplishment are reported they should provide a firm basis for a major advance in understanding of the lower atmosphere of Venus. Only a limited amount of information is yet available through Russian radio and press releases on the direct measurements of atmospheric properties. One can, however, use the information on Venera 4's entry and descent trajectory to provide further insight into those atmospheric data. After summarizing briefly the information available from the Venera-4 probe we shall describe the model atmospheres that we have constructed on the basis of these data and show how trajectory calculations strengthen the validity of these models.

Regarding the data used in this analysis, in certain instances numerical values quoted (*1, 2*) for some of the quantities differ slightly; in all such cases the later values (*2*) have been used, since they presumably reflect more detailed analysis of the data.

The probe was "almost" spherical; its diameter was 1 meter and it weighed 383 kilograms. The point of entry into the atmosphere was near the equator and 1500 ± 500 kilometers from the terminator on the dark side. From an entry velocity of 10.7 kilometers per second, aerodynamic deceleration slowed the probe to 300 meters per second, at which point a drogue parachute was deployed. After subsequent deployment of the main parachute which reduced the velocity to about 10 meters per second, the antenna systems were extended, a radio altimeter was switched on, and the radio began to transmit to Earth.

At an altitude of 26 kilometers, as measured by the radio altimeter, samples of gas were drawn into five gas-analyzer tubes. In each tube the amount of gas absorbed was determined by measurement of the reduction in pressure by a chemical capable of absorbing a selected component of the gas mixture. The ambient pressure measured at this point by an aneroid barometer was 0.684 atmosphere; the temperature, determined by two resistance thermometers, was 313° ± 10°K. After 347 seconds, at an altitude of 23 kilometers, the remaining six gas-analyzers received their samples; the pressure at this altitude was 1.98 atmospheres and the temperature was 353° ± 10°K. The analyses of gases gave a composition of 90 to 95 percent carbon dioxide (also announced as 90 percent with less than 10 percent error), 0.1 to 0.7 percent water vapor, more than 0.4 percent oxygen, and less than 1.5 percent oxygen and water vapor combined. From the last three values one can deduce that the oxygen content was between 0.4 and 1.4 percent—which contrasts with the announced (*2*) oxygen content of between 0.4 and 0.8 percent. An analyzer having a nitrogen threshold of 7 percent gave no indication of that gas.

During descent the variation in temperature was "almost" linear, with a mean gradient of about 10°K per kilometer. Near the surface the temperature was 543° ± 7°K; the pressure, 20 ± 2 atmospheres; and the descent velocity, about 3 meters per second. Radio transmission ceased 94 minutes after the first measurements were taken at the 26-kilometer altitude.

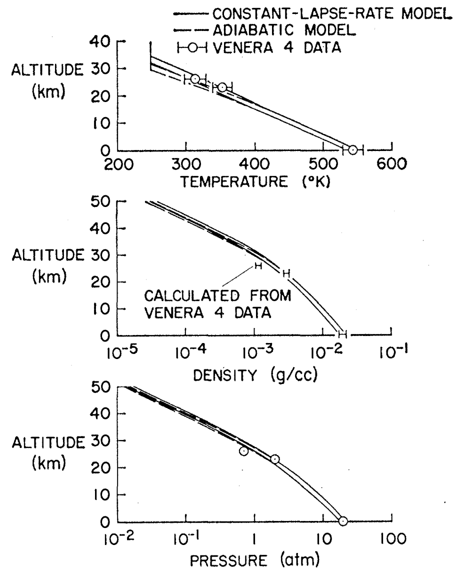

Fig. 1. Atmospheric profiles constructed from Venera-4 data.

Two model atmospheres were fitted to these data. Since the temperature variation with altitude was "almost" linear, the first model selected was a constant-lapse-rate model. The linear temperature profiles and their associated lapse rates are based on the temperature values at 26 kilometers and on the surface. The upper and lower temperature models were obtained by connection of Venera 4's upper and lower limiting temperatures, respectively, at the two altitudes. The limiting values of surface density were calculated from the upper and lower temperature values and the lower and upper pressure values, respectively, on the assumption that the composition was 95 percent CO_2 and 5 percent N_2. The altitude profiles of density and pressure were then calculated by use of well-known constant-lapse-rate relations.

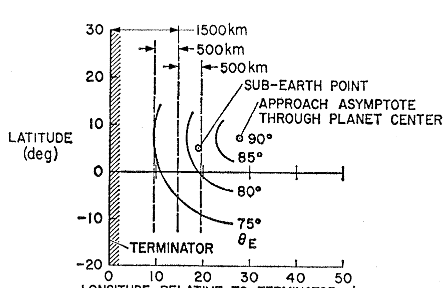

Fig. 2. Location on Venus of Venera 4's point of entry.

An adiabatic model also was selected for which the lapse rate varies with altitude because of the variation with temperature and pressure of the specific heat of CO_2. The lapse-rate values were based on a 100-percent CO_2 composition by use of reported (*3*) properties of CO_2. Profiles of temperature, density, and pressure were then calculated from only the Venera-4 surface data and the adiabatic relations (Fig. 1).

Generally the models fit the data reasonably well, but the gradients of temperature, density, and pressure, in the altitude range from 23 to 26 kilometers, determined by Venera 4 are appreciably greater than for the model atmospheres. The average density scale height over this range of altitude as calculated directly from the Venera-4 pressure and temperature points is 3.4 kilometers, whereas the constant-lapse-rate and adiabatic models give 8.5 and 7.6 kilometers, respectively. These differences are probably indications of the failure of our simple models to fit what is very probably a complex atmospheric structure.

To extend the model atmospheres to altitudes covering the region of sensible aerodynamic effects, the Mariner-V scale-height value of 5.4 ± 0.2 kilometers was used (*3*). For purposes of model construction, it was assumed that the atmosphere could be represented by an isothermal stratosphere whose temperature was given by the Mariner-V scale-height value and the mean molecular weight of a 95:5 mixture of CO_2 and N_2; the stratospheric temperature yielded by this method is 249°K. The tropopause altitude was determined by extension of the lower-atmosphere temperature profiles to an altitude at which the stratospheric temperature was reached; this calculation gives tropopause altitudes of 32.7 and 35.1 kilometers for the constant-lapse-rate models, and 30.2 and 32.2 kilometers for the adiabatic models.

We turn now to the trajectory calculations and their use for evaluation of the atmosphere models. We have divided these calculations into a high-speed phase, from entry to a velocity of 300 meters per second (parachute-deployment velocity), and a descent phase covering the equilibrium descent on the main parachute. Calculations for the high-speed phase are valuable for determination of the point at which a velocity of 300 meters per second was reached, for comparison with the 26-

Table 1. Venera-4 entry and descent parameters.

Limit	Parachute-deployment altitude (km)	Time from 26 km to		Velocity at surface (m/sec)
		23 km (sec)	Surface (min)	
Constant-lapse-rate model				
Upper	34.5	330	87.4	3.1
Lower	33.2	322	84.6	3.2
Adiabatic model				
Upper	33.7	328	87.0	3.0
Lower	32.4	325	85.2	3.0
Venera-4 data				
		347	94	3

kilometer altitude stated by the Russians to have been the point of the first measurements. Unfortunately this calculation is insensitive to the atmosphere structure and therefore does not offer a check on the structure above this point. As noted by Seiff (*4*) the Allen-Eggers expression for velocity V during ballistic entry can be written

$$V = V_E{}^e - \frac{C_D A}{m} \times \frac{p}{2g \sin \theta_E}$$

Here C_D is the drag coefficient of the entering probe, A is its reference area, m is its mass, V_E is its entry velocity, θ_E is the angle of its flight path relative to the local horizontal, g is the acceleration due to gravity of the planet, and p is the atmospheric pressure at the point in question. Clearly the only atmospheric parameter involved is the pressure; thus the equation can be used for calculation of the pressure at which the velocity of 300 meters per second was reached. [One should note that "the decelerating and main parachutes were made operative on command from the external pressure transducer" (*1*).] By reference to the model atmospheres the altitude at which the parachute opening was initiated can be estimated and compared with the 26-kilometer altitude at which measurements began.

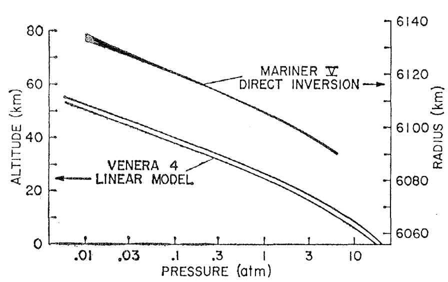

Fig. 3. Comparison of Mariner V's S-band occultation results with atmospheric-pressure models based on Venera 4.

To make the calculation one must know the entry velocity and flight-path angle. From the known dates of departure from Earth and arrival at Venus, the approach hyperbolic excess-velocity vector can be determined: its magnitude of 3.16 kilometers per second gives an entry velocity of 10.7 kilometers per second at an altitude of approximately 150 kilometers. The flight-path angle can be determined from the orientation of this approach-velocity vector and from the location of the point of entry (*1*). The relative geometry of these two quantities is shown in Fig. 2, together with the location of the sub-Earth point. Incidently, since the probe communicated with Earth directly, the target-entry point was probably the sub-Earth point which lies within the landing region (Fig. 2). From Fig. 2 we conclude that the flight-path angle of entry was 78 $\pm$ 4 degrees.

With these values for entry conditions and a hypersonic-drag coefficient of 0.94 appropriate to a sphere, one can calculate the atmospheric pressure at which the velocity reached 300 meters per second—0.317 atmosphere. In turn this value gives parachute-deployment altitudes for the various atmospheric models (Table 1); these values were verified within a few tenths of a kilometer by digital-computer calculations taking into account many details not included in the Allen-Eggers approximation. One can see that the values range from 6.4 to 8.5 kilometers above the point at which the first measurements were made. Since the parachute system used both a drogue and a main parachute, some loss in altitude may be expected between deployment of the drogue and stable descent on the main parachute, depending on the drag of the drogue, the time between deployments of drogue and main chute, and the duration of reefing (if any) of the main chute. The losses in altitude implied (Table 1) appear to be quite compatible with the Venera-4 results.

In the descent phase of the trajectory calculations one can calculate descent time and velocity as functions of altitude for each of the model atmospheres, using the quoted descent velocity of 10 meters per second at an altitude of 26 kilometers as an initial condition. Comparison of these results with the Venera-4 data provides a good test of the model atmospheres, since significant departures from the true atmosphere, especially in the higher-density regions, will have significant effects on duration of descent (Table 1). The calculated values are all within 10 percent of the announced values. The initial descent velocity of 10 meters per second was announced to two significant figures only, and a decrease of 0.5 meter per second in that value would increase the time to the surface by about 4.5 minutes. Thus the results shown in Table 1 not only support the validity of the atmospheric models but also are completely consistent with the Russian report that the probe survived until impact on the surface. If it did not survive, one must believe not only that the radio-altimeter measurement of 26 kilometers was low, but also that it was coincidental that the probe expired at a distance below the first data point almost precisely equal to the incorrect altimeter reading.

It is of interest to compare the Venera-4 results to the Mariner-V S-band occultation results (*4*) obtained closer to the antisolar direction but at about 37-degree north latitude. Comparing the pressure data, we have plotted (Fig. 3) results from our linear-lapse-rate models, based on the Venera-4 data, together with the direct-inversion results of Mariner V. We have assumed in aligning the two ordinates that the radius of the planet is 6056 kilometers (*6*). Clearly the two results are in disagreement by some 24 kilometers in altitude, or by more than one order of magnitude in pressure. Both the Mariner-V trajectory analysis and the radar determination of the planet's equatorial radius are too accurate to allow errors of the order of 20 kilometers, and the discrepancies between the two sets of data must be considered still unresolved.

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