

## Role of Phase Transitions in a Dynamic Mantle

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(Received 1975 February 10)\*

### *Summary*

The interaction of solid–solid phase transitions with convection in the Earth's mantle involves, for univariant systems: (1) effects of latent heat and advection of ambient temperature on the position of the phase boundary and on its associated body force, and (2) the coupling of latent heat with the ordinary thermal expansivity of the material. For divariant systems, an effective thermal expansion coefficient and a modified adiabatic temperature gradient may be defined for the phase transition zone. Linear stability theory for a fluid layer with a univariant phase change is reviewed and applied to the endothermic spinel–oxide transformation. The theory of the stability of a fluid layer with a divariant phase transformation is developed and critical Rayleigh numbers are given for a model of the olivine–spinel transition. Of special interest is the case where the Earth's temperature gradient exceeds the adiabatic temperature gradient outside the phase transition zone but is smaller than the increased adiabatic temperature gradient in the two-phase olivine–spinel region. The thermal structure of the descending lithosphere is calculated, including the effects of frictional heating on the slip zone and of the olivine–spinel and spinel–oxide transitions; temperature contrasts of 700 °K can exist between the slab and adjacent mantle at 800 km depth. The net body force on the descending slab due to thermal contraction and the major mineralogical phase changes is downward. The olivine–spinel transition may be responsible for the tensional focal mechanisms of intermediate depth earthquakes while the spinel–oxide transformation may be related to the compressional focal mechanisms of deep earthquakes.

### **Introduction**

From both seismological (Anderson 1967; Johnson 1967; Archambeau, Flinn & Lambert 1969; Wiggins & Helmsberger 1973) and high pressure mineralogical (Aki-moto & Fujisawa 1968; Ringwood 1970; Bassett & Ming 1972; Kumazawa *et al.* 1974; Ming & Bassett 1975) evidence, it is generally agreed that there are at least two major phase transitions in the Earth's mantle. They are believed to be the changes of phase from olivine to spinel at about 350–400 km depth and from spinel to a post spinel structure at about 650 km depth, primarily as a result of the large increase in pressure with depth in the Earth's interior. Since changes in density and the release or absorp-

\* Received in original form 1974 September 20.

tion of latent heat accompany phase transformations, the character of motions in the Earth's mantle can be profoundly affected.

The importance of mineralogical phase changes was first indicated by Birch (1952) who argued, on the basis of the theory of elastic properties, for the existence of phase transitions between 400 and 900 km depth. Vening Meinesz (1962) carried out an analysis for moving fluid parcels undergoing a univariant phase change in a transition zone and found that the phase change could promote instability. Both Knopoff (1964) and Verhoogen (1965) discussed the problem of convection through a phase change and concluded that the transition would act as an obstacle to the flow. The mathematical linear stability analysis of a fluid layer with a univariant phase change has been carried out by Schubert, Turcotte & Oxburgh (1970), Busse & Schubert (1971) and Schubert & Turcotte (1971). Schubert *et al.* (1970) applied this theory to the olivine–spinel phase change and found that it could have a destabilizing effect in the presence of a negative temperature gradient. The stability analysis, taking into account both the ordinary Rayleigh instability associated with thermal expansion and a phase change instability driven by the density difference between the phases, was carried out by Schubert & Turcotte (1971), who also found that the olivine–spinel phase change in the presence of a negative temperature gradient may enhance deep mantle convection.

Ringwood (1972) pointed out that an enhanced adiabatic gradient in the two-phase transition region would tend to inhibit mantle convection currents.

We show in this paper that, although the adiabatic gradient in the olivine–spinel phase change zone has a stabilizing influence, overall the phase transformation may promote instability. Finite-amplitude numerical calculations (Richter 1973a) show that convection through a univariant model of the olivine–spinel phase change is possible for subcritical Rayleigh numbers and, at higher Rayleigh numbers, convection is enhanced compared to a fluid without a phase change. Peltiér (1973) treated the stability problem for a layer of fluid containing a univariant phase transition and with variable physical properties, such as viscosity and thermal conductivity; his results are in agreement with those obtained earlier by Schubert & Turcotte (1971).

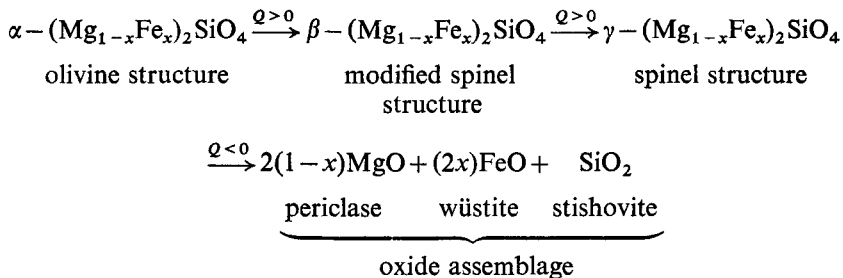
In addition to the phenomenon of stability, we must consider the finite-amplitude effects of phase transformations on the descending lithospheric slab. The influence of the heat liberated by the olivine–spinel phase change on the temperature structure of the downgoing slab has been included by Hasebe, Fujii & Uyeda (1970), Turcotte & Schubert (1971, 1973) and Toksöz, Minear & Julian (1971). The idea that phase changes can provide a substantial amount of downward body force to the sinking lithosphere has been emphasized by Schubert & Turcotte (1971), Turcotte & Schubert (1971) and Griggs (1972). The additional body force due to the elevation of the phase boundary in the relatively cold slab is comparable to the body force due to thermal contraction. Here, we consider the further influence of the spinel–post-spinel phase change on the thermal structure and body force of the downgoing slab. The possible importance of phase-change-induced stresses in the descending lithosphere has been speculated upon by Isacks & Molnar (1971) on the basis of focal mechanism solutions of intermediate and deep earthquakes. Smith & Toksöz (1972), basing themselves on numerical calculations of stress distribution in the descending slab, have reported that the olivine–spinel transition induced local stress concentrations in its vicinity; the slab tends to be in tension above 350 km and in compression below this depth in agreement with the findings of Isacks & Molnar (1971). Our calculation of the body force in the downgoing slab, which includes the spinel–post-spinel phase change, yields a distribution which implies similar tensional and compressional stresses above and below the 350-km discontinuity.

The present paper has two major objectives. First, we extend the analyses of Schubert *et al.* (1970), Schubert & Turcotte (1971) and Busse & Schubert (1971) on the stability of fluid layers containing univariant phase transitions to the case where

the phase transformations are divariant in nature, as are the mineralogical phase changes in the Earth (Verhooogen 1965). It is demonstrated that the most important characteristics of the divariant olivine-spinel system are an effective coefficient of volume expansion some one to two orders of magnitude larger than single phase thermal expansion coefficients thus tending to enhance convective instability, and an adiabatic temperature gradient in the transition region larger than single phase gradients, thus tending to promote stability. The effect on layer stability of phase boundary distortion or displacement does not appear in the linear stability analysis of a divariant phase transformation. The phenomenon is present in the system with univariant phase changes and in the case of finite amplitude motions through any type of phase change, e.g. the motion of the descending slab through the 400 km olivine-spinel transition.

Our second objective is to apply the univariant and divariant stability analyses, and the analysis of the finite amplitude motion of the descending slab through a phase change to the two major phase transitions. Recent experimental work (Bassett & Ming 1972; Kumazawa *et al.* 1974; Ming & Bassett 1975) has shown that the spinel-post-spinel phase change involves the decomposition of spinel to its component oxides. If the thermochemical calculations of Ahrens & Syono (1967) adequately describe the thermodynamics of this transition, then its endothermic character leads to effects on convection which contrast interestingly with those of the exothermic olivine-spinel transformation. We will assume in this paper that the spinel-oxide transition is indeed endothermic. With this assumption, the spinel-oxide transition merits special discussion. If the spinel-oxide transition were exothermic, the phase change would influence convection in a manner analogous to the olivine-spinel transition.

The following sequence of reactions summarizes the series of phase changes that olivine undergoes at increasing depths in the Earth's interior:



The parameter  $x$ , which represents the mole fraction of fayalite in olivine, is believed to lie between 0.15 and 0.25 on the basis of petrological and seismological data (Ahrens 1973; Anderson 1970). The latent heat of reaction is denoted by  $Q$ ; for  $Q > 0$  the reaction is considered exothermic and for  $Q < 0$  it is considered endothermic. Each reaction yields a phase of higher density.

### Univariant phase change stability

In this section we review the physical principles underlying the theory of the stability of a layer of Boussinesq fluid containing two phases with a univariant phase change boundary (Schubert *et al.* 1970; Schubert & Turcotte 1971; Busse & Schubert 1971). Although the solid-solid transitions in the earth are polyvariant in nature, the univariant system is a relevant approximation because of the relatively small width of transition zones as compared with their depths and the largely forsterite composition of the upper mantle. Further, an important aspect of the physics of convection through a phase change, namely the displacement of the phase boundary, is

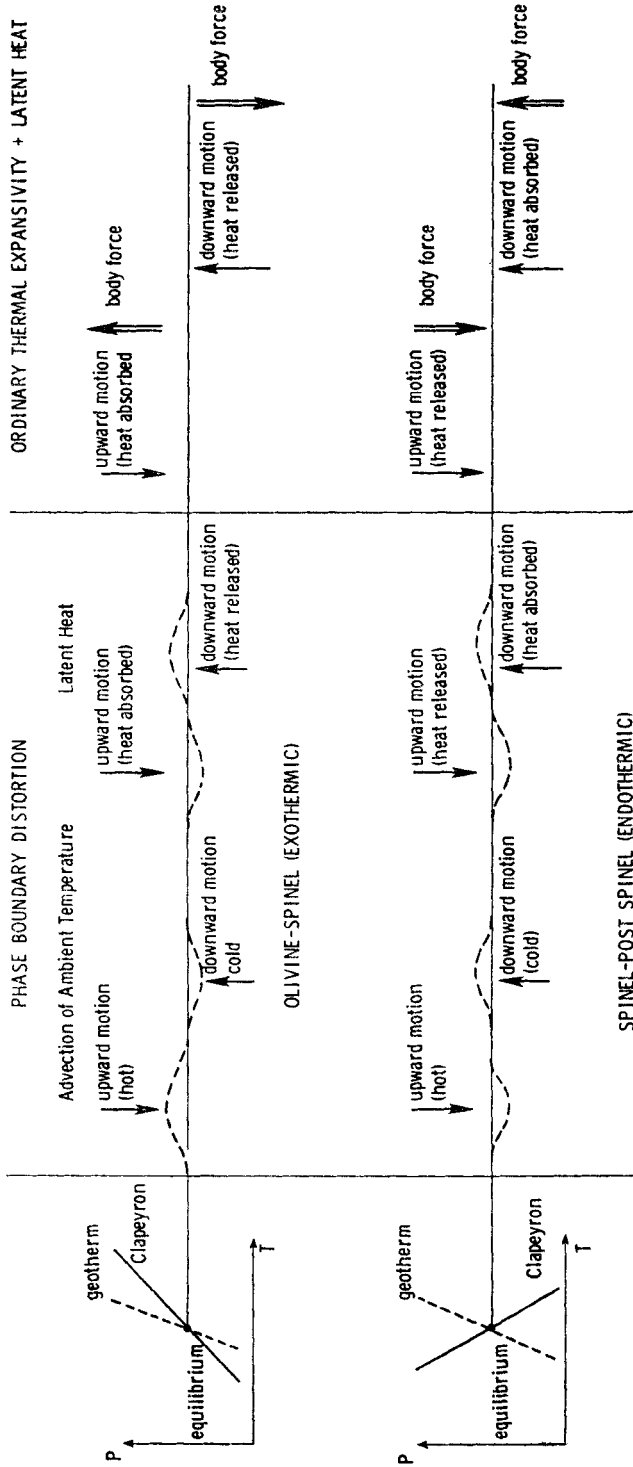


FIG. 1. The stabilizing and destabilizing mechanisms associated with exothermic and endothermic univariant phase changes. The dynamical effects of the transitions are referred to the  $p-T$  diagram on the left, which shows the phase equilibrium or Clapeyron curve (solid) and the ambient temperature gradient or geotherm (dashed). The directions of upward and downward motion point to lesser and greater pressures, respectively. Hot and cold denote relative temperatures associated with the ambient temperature gradient. The direction of the body force represents the thermal expansion or contraction effect on a fluid parcel due to the release or absorption of latent heat. The long horizontal lines indicate the equilibrium positions of the phase change interface, while the dashed portions describe the sense of distortion (in pressure co-ordinates).

	Phase Boundary Distortion		Ordinary Thermal Expansivity + Latent Heat
	Advection of Ambient Temperature	Latent Heat	
Olivine-Spinel (Exothermic)	Destabilizing	Stabilizing	Stabilizing
Spinel-Post Spinel (Endothermic)	Stabilizing	Stabilizing	Destabilizing

FIG. 2. Summary of the stabilizing and destabilizing effects of exothermic and endothermic univariant phase changes associated with phase boundary distortion and ordinary thermal expansivity plus latent heat.

brought out by considering univariant transitions; in a later section we reconsider the stability problem from the point of view of a divariant system.

From Gibbs phase rule of equilibrium thermodynamics, the univariant phase change equilibrium curve in temperature  $T$  and pressure  $p$  space, i.e. the Clapeyron curve, provides a unique relationship between  $p$  and  $T$ . The slope of the Clapeyron curve  $\gamma$  is, according to the Gibbs–Duhem equation (Guggenheim 1967)

$$\gamma = \left( \frac{dp}{dT} \right)_c = \frac{Q\rho_1\rho_2}{T\Delta\rho}, \quad (1)$$

where  $\Delta\rho = \rho_2 - \rho_1$  is the change in density at the phase transition (the subscripts 1 and 2 refer to the upper and lower phases, respectively), and  $Q$  is the latent heat required per unit mass to change material of phase 2 into that of phase 1. For the olivine–spinel phase change, the dense phase (spinel) lies beneath the light phase (olivine), heat is evolved when olivine changes into spinel, and  $Q$ ,  $\Delta\rho$ , and  $\gamma$  are all positive. In the case of the spinel–post-spinel transition, the light phase (spinel) also lies above the heavy phase and  $\Delta\rho > 0$ . We assume, following Ahrens & Syono (1967), since the transition involves a breakdown to the component oxides (Bassett & Ming 1972; Kumazawa *et al.* 1974; Ming & Bassett 1975), that the reaction is endothermic when spinel disproportionates to the oxides, i.e.  $Q$  and thus  $\gamma$  are negative.

The system is assumed to be in thermodynamic equilibrium so that the location of the phase boundary is determined by the intersection of the Clapeyron curve with the pressure–temperature curve for the fluid layer. In the perturbed state the phase boundary will be displaced from its initial position. If the less dense phase lies above the more dense phase, the slope of the pressure–temperature curve (assumed positive as in the case of the Earth) exceeds the slope of the Clapeyron curve, for  $\gamma$  positive.

The stability, or instability, of a univariant phase transition is determined by a number of competing effects associated with the ordinary thermal expansivity of the material and the displacement of the phase boundary coupled with the density difference between the phases. Consider the situations for the olivine–spinel (exothermic) and spinel–post-spinel (endothermic) transitions as shown in Fig. 1. The Clapeyron curves are drawn solid while the ambient pressure–temperature curves are dashed. The Earth’s interior has a negative temperature gradient, i.e.  $T$  decreases upward. On a  $p$ – $T$  plot the geotherm has a positive slope. We proceed to discuss the stabilizing and destabilizing mechanisms associated with the phase changes, as

illustrated in Fig. 1 and summarized in Fig. 2. The ordinary Rayleigh convective instability mechanism associated with a single-phase fluid heated from below and cooled from above will not be explicitly discussed; the effect is included, of course, in our quantitative stability computations.

#### *Ordinary thermal expansivity and latent heat*

A parcel of fluid moving downward through the olivine–spinel (exothermic) phase change is heated by latent heat release. It thus experiences an upward, stabilizing buoyancy force because of ordinary thermal expansion. In contrast, a parcel moving downward through the spinel–post-spinel (endothermic) phase transition cools by supplying the requisite latent heat, contracts due to thermal expansivity and is subjected to a downward destabilizing body force. The situations, depicted in Figs 1 and 2, show that latent heat release or absorption when coupled with thermal expansion or contraction influences stability in opposite ways for the two major phase transitions considered here.

#### *Phase boundary distortion and latent heat*

The release or absorption of latent heat influences the stability of a univariant phase change in another way, namely by contributing to the displacement of the phase boundary. Because of the heat evolved (absorbed) when material moves downward through the olivine–spinel (spinel–post-spinel) phase change, the local temperature tends to increase (decrease) and since the phase change interface must remain on the Clapeyron curve, the boundary is displaced downward to higher pressure (Fig. 1). A vertical column of material containing more of the light phase and weighing less than an ambient undisturbed column, experiences an upward stabilizing hydrostatic pressure head (Fig. 2). An analogous argument applies to material moving upward through the phase transition. The situation is summarized in Figs 1 and 2; latent heat release, when coupled with both thermal expansivity and phase boundary distortion is a stabilizing influence for the olivine–spinel transition. For the spinel–post-spinel transformation latent heat coupled with phase boundary distortion provides a stabilizing effect; when latent heat is considered together with ordinary thermal expansion its influence is destabilizing.

#### *Phase boundary distortion and advection of ambient temperature*

Material particles moving through the phase boundary induce local temperature perturbations and thus phase boundary displacement because the particles tend to retain the hotter or colder ambient temperature from below or above the equilibrium phase boundary location. Parcels moving upward (downward) induce positive (negative) temperature perturbations at the phase boundary because the ambient temperature increases with depth or pressure. Since the phase boundary must remain on the Clapeyron curve, such a positive (negative) thermal perturbation causes the phase boundary to distort downward (upward), i.e. opposite to the direction of material transport in the case of the olivine–spinel transition since  $\gamma$  is positive. However, for the spinel–post-spinel transition, for which  $\gamma$  is negative, the phase boundary is displaced in the same sense as the motion of material through the transition. By considering the weight of a vertical column through the displaced phase boundary relative to that of an ambient fluid column, it is clear that phase boundary distortion which opposes material motion is destabilizing while interface displacement which is in the same sense as the material transport is stabilizing. Figs 1 and 2 illustrate how thermal perturbations caused by advection of the mean temperature lead to instability in the case of the olivine–spinel transformation and stability in the case of

the spinel–post-spinel transition. Advection of the ambient temperature by the descending slab and phase boundary displacement therein provides an important example of this effect in mantle convection.

The conditions under which a phase change will enhance or hinder solid state convection are thus seen to involve a competition between several opposing effects. Only quantitative stability computations can determine which of the physical effects predominate. It is interesting that phase boundary distortion provides both stabilizing and destabilizing tendencies for the olivine–spinel transition while for the spinel–post-spinel case it is wholly stabilizing.

*Quantitative stability computations*

The results of the linearized theory of univariant phase change stability (Schubert & Turcotte 1971) can be discussed in terms of the following dimensionless parameters

$$R_\beta = \frac{\alpha(\beta - \beta_a)gD^4}{\kappa\nu}, \tag{2}$$

$$R_Q = \frac{\alpha g D^3 (Q/c_p)}{\kappa\nu}, \tag{3}$$

$$S = \frac{\Delta\rho/\rho}{\alpha D((\rho g/\gamma) - \beta)}, \tag{4}$$

where  $\alpha$  is the ordinary coefficient of thermal expansion,  $\beta$  is the magnitude of the

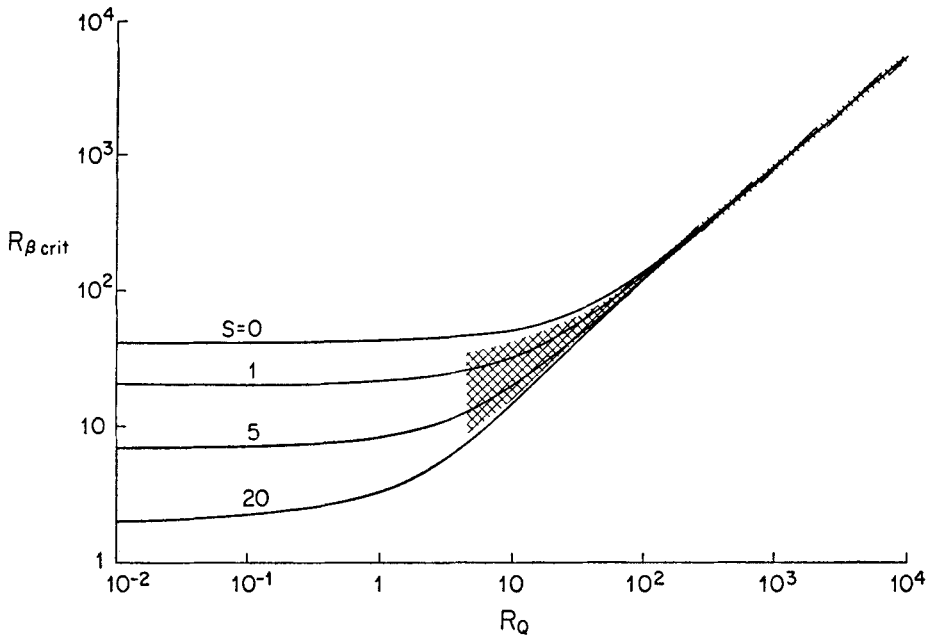


FIG. 3. The minimum Rayleigh number  $R_{\beta_{crit}}$  for convection through the univariant exothermic phase boundary as a function of the latent heat parameter  $R_Q$  for various values of the phase boundary distortion parameter  $S$ . The cross-hatched region corresponds to the parameter values most representative of the olivine–spinel transition in the Earth’s mantle.

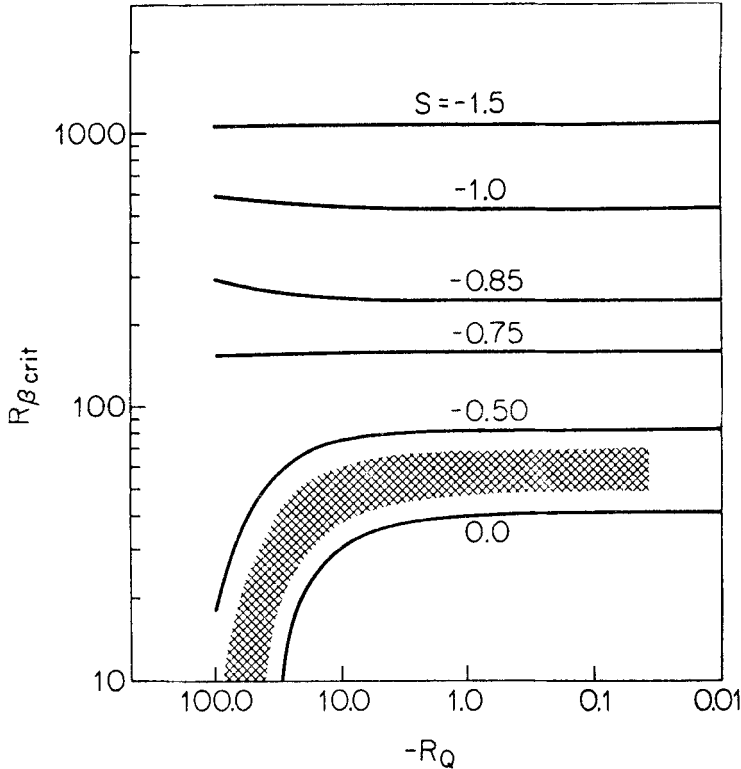


FIG. 4. The minimum Rayleigh number  $R_{\beta \text{crit}}$  for convection through the univariant endothermic phase boundary as a function of  $R_Q$  for various values of  $S$ . The cross-hatched region corresponds to the parameter values most characteristic of the spinel-oxide transition in the Earth's mantle.

ambient negative temperature gradient (geothermal gradient), and  $\beta_a$  is the adiabatic temperature gradient for a univariant system given by

$$\beta_a = \left( \frac{\partial \rho^{-1}}{\partial T} \right) \frac{\rho g T}{c_p}. \quad (5)$$

The adiabatic temperature gradient is assumed to have the same value for both phases; it is to be evaluated at the position of the undisturbed phase boundary. The parameter  $g$  is the acceleration of gravity,  $\rho$  is the density which is approximately equal to  $\rho_1$  and  $\rho_2$ , i.e.  $\Delta \rho \ll \rho \approx \rho_1 \approx \rho_2$ ,  $2D$  is the thickness of the fluid layer (the phase boundary is placed at the centre of the layer),  $\kappa$  is the thermal diffusivity,  $\nu$  is the kinematic viscosity, and  $c_p$  is the ordinary specific heat at constant pressure. We assume that  $\kappa$ ,  $\nu$ ,  $c_p$  and  $\alpha$  have the same values for both phases.

The parameter  $R_\beta$  is the ordinary Rayleigh number; when  $R_\beta$  exceeds a certain critical value,  $R_{\beta \text{crit}}$ , convective instability sets in. Alternatively, the critical Rayleigh number provides a minimum value of the superadiabatic temperature gradient above which the system will convect. The parameter  $S$  is the phase boundary displacement parameter; it represents the ratio of the fractional density change in the phase transition to the fractional density change associated with thermal expansion. For the olivine-spinel phase transition,  $S$  is a positive quantity whereas for the spinel-post-spinel transformation  $S$  is negative. The parameter  $R_Q$  is of the form of a Rayleigh number based on the temperature difference ( $Q/c_p$ ); it measures the influence of the



latent heat released in the phase transition. For the olivine–spinel transition  $R_Q$  is positive while for the spinel–post-spinel change it is negative.

We have calculated critical Rayleigh numbers for the two major mineralogical phase changes from the eigenvalue equation given by Schubert & Turcotte (1971), which is based upon stress-free, constant temperature, rigid boundaries for the fluid layer. Because the physical, thermodynamic, and rheological properties of the mantle are not known accurately, we computed values of  $R_{\beta_{\text{crit}}}$  as a function of  $R_Q$  with  $S$  as a parameter. The results are shown in Fig. 3 for the olivine–spinel phase change and in Fig. 4 for the spinel–post-spinel transition. The cross-hatched regions represent those we consider to be most representative of the Earth's mantle.

### Univariant olivine–spinel stability

To assess the relative importance of the olivine–spinel (or spinel–post-spinel) phase change on fluid layer stability we must compare  $R_{\beta_{\text{crit}}}$  for a fluid in which the transition occurs to the critical Rayleigh number  $R_{\beta_{\text{crit}}}^*$  for a single-phase fluid layer. For  $R_Q = S = 0$ , or no phase change, we recover the case of ordinary Rayleigh instability for which  $R_{\beta_{\text{crit}}}^* = (27\pi^4)/(2^6) = 41.094$  (Chandrasekhar 1961). Fig. 3 shows the stabilizing effect of latent heat release at the phase change interface; as the parameter  $R_Q$  increases, the critical Rayleigh number for a fixed value of  $S$  also increases though rather slowly for  $R_Q < 10$ . For  $R_Q$  sufficiently large, the critical Rayleigh number becomes insensitive to the value of  $S$  and it eventually exceeds the critical Rayleigh number of 657.504 (Chandrasekhar 1961). We find from Fig. 3 that  $R_{\beta_{\text{crit}}}$  decreases as  $S$  increases for fixed  $R_Q$ . This reflects the fact that as  $S$  increases, phase boundary distortion coupled with the fractional density change associated with the phase transition becomes increasingly important as compared with the density change associated with ordinary thermal expansion, and the phase change plays a more significant role in driving the instability, thus reducing the critical Rayleigh number.

Table 1 lists the values of those parameters relevant to the computation of  $R_Q$  and  $S$  for the olivine–spinel phase change in the Earth's upper mantle. The resultant ranges in values of  $R_Q$  and  $S$  are indicated by the cross-hatched region of Fig. 3. Many possible earth models with the olivine–spinel phase change are more unstable to convection than a single-phase model without the transition. This can be seen in the alternate presentation of the results of the stability computations shown in Fig. 5. The  $R_{\beta_{\text{crit}}}$  vs  $R_Q$  plot can be transformed into a graph of  $(\beta - \beta_a)_{\text{crit}}$  vs  $v$ , i.e. a graph

**Table 1**

#### *Parameters for the stability analysis of the univariant olivine–spinel transformation*

$3 \times 10^{-5} \text{ }^\circ\text{K}^{-1} \lesssim \alpha \lesssim 3.5 \times 10^{-5} \text{ }^\circ\text{K}^{-1}$	Jacobs (1956), Skinner (1966), Schubert, Turcotte & Oxburgh (1969)
$0.08 \lesssim \Delta\rho/\rho \lesssim 0.10$	Akimoto & Fujisawa (1968), Ringwood & Major (1970)
$30b/\text{ }^\circ\text{K} \lesssim \gamma \lesssim 62b/\text{ }^\circ\text{K}$	Akimoto & Fujisawa (1968), Ringwood & Major (1970)
$1800 \text{ }^\circ\text{K} \lesssim T \lesssim 1900 \text{ }^\circ\text{K}$	Schubert <i>et al.</i> (1969)
$10^{22} \text{ cm}^2 \text{ s}^{-1} \lesssim \nu \lesssim 10^{24} \text{ cm}^2 \text{ s}^{-1}$	McKenzie (1967), Stocker & Ashby (1973), Cathles (1971), Brennen (1974)
$10^{-2} \text{ cm}^2 \text{ s}^{-1} \lesssim \kappa \lesssim 2 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$	Schatz & Simmons (1972)
$300 \text{ km} \lesssim D \lesssim 400 \text{ km}$	Archambeau <i>et al.</i> (1969), Wiggins & Helmberger (1973), Massé (1974)
$1 \text{ }^\circ\text{K km}^{-1} \lesssim \beta \lesssim 5 \text{ }^\circ\text{K km}^{-1}$	Schubert <i>et al.</i> (1969)
$c_p \approx 1.25 \times 10^7 \text{ erg g}^{-1} \text{ }^\circ\text{K}^{-1}$	Jacobs (1956)
$0.50 \lesssim S \lesssim 18$	
$5 \lesssim R_Q \lesssim 6 \times 10^3$	

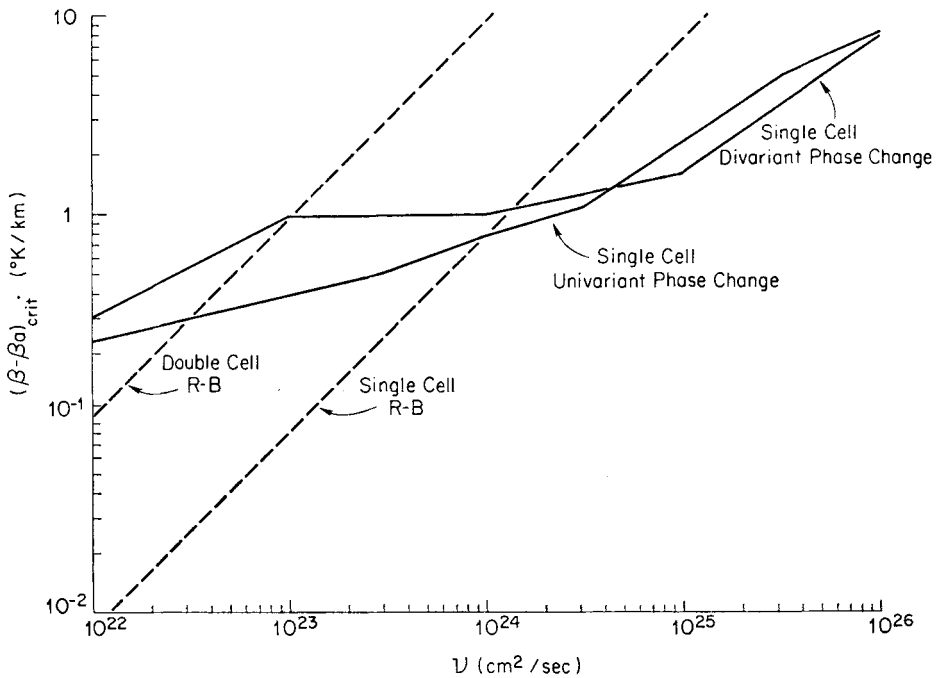


FIG. 5. The minimum superadiabatic temperature gradient  $(\beta - \beta_a)_{\text{crit}}$  for instability in the Earth's mantle as a function of kinematic viscosity  $\nu$ . The dashed lines represent the stability curves for single-cell and double-cell convection in a mantle without a phase change (Rayleigh-Bénard stability). The solid lines represent the stability curves for a mantle with the olivine-spinel phase change, on the basis of both the univariant and the divariant stability theories. For a given value of  $\nu$ , the curve with the smallest value of  $(\beta - \beta_a)_{\text{crit}}$  represents the most destabilizing mechanism, according to linear theory.

of minimum superadiabatic temperature gradient required for the onset of convection *vs* kinematic viscosity, for a particular set of parameter values for the other quantities appearing in the dimensionless parameters. In the construction of the 'single-cell univariant phase change' curve of Fig. 5, we use the following values appropriate to the olivine-spinel transformation:  $D = 400$  km,  $\Delta\rho/\rho = 0.08$ ,  $\gamma = 40$  bars/K,  $Q = 40$  cal/g,  $\alpha = 3 \times 10^{-5}$  K $^{-1}$ ,  $g = 10^3$  cm s $^{-2}$  and  $\beta\gamma/\rho g \ll 1$  which yields  $S = 0.76$ . The 'single cell R-B' line of Fig. 5 is the stability curve for onset of Rayleigh-Bénard convection in a single phase fluid with thickness  $2D$ . The 'double cell R-B' curve of Fig. 5 is the stability boundary for the onset of ordinary Rayleigh-Bénard convection in a single-phase fluid layer of thickness  $D$ . This stability boundary is relevant to the possibility that the onset of convection might occur as double-cell convection above and below the phase change rather than as single-cell convection through the transition. Also shown in Fig. 5 is the stability curve for single-cell convection through the phase change based on a divariant theory of stability to be discussed later. The figure shows that for  $\nu$  less than about  $3 \times 10^{22}$  to  $10^{23}$  cm $^2$  s $^{-1}$ , double-cell convection requires a somewhat smaller superadiabatic temperature gradient to occur than single cell convection through the phase change. For  $\nu$  between  $3 \times 10^{22}$  or  $10^{23}$  and  $10^{24}$  cm $^2$  s $^{-1}$ , convection through the phase change is the preferred mode although the layer would be more unstable if the phase change were absent. If  $\nu$  is larger than about  $10^{24}$  cm $^2$  s $^{-1}$  the phase change makes the layer more unstable to single-cell convection than if the transition were not present.

*Univariant spinel–post spinel stability*

Critical Rayleigh numbers for negative values of  $S$  and  $R_Q$  as appropriate for the spinel–post spinel phase change are given in Fig. 4. The cross-hatched region delineates the range of plausible earth models defined by the parameter values given in Table 2. Within this region,  $R_{\beta_{crit}}$  can be no more than twice the value of  $R_{\beta_{crit}}^*$ , the ordinary critical Rayleigh number for single-phase fluid instability. It is possible for  $R_{\beta_{crit}}$  to be less than  $R_{\beta_{crit}}^*$  for some reasonable earth models so that the spinel–post-spinel transformation would make the layer more unstable to convection than it would be if the phase change did not exist.

From Fig. 4 we see that the effect of  $|S|$  and  $|R_Q|$  on  $R_{\beta_{crit}}$  are opposite to their influence on the olivine–spinel transition. This is clear from the fact that as  $|S|$  increases in magnitude, i.e. as phase boundary distortion becomes more important, the configuration becomes more stable. For the case  $S = 0$  there is no phase boundary displacement and the latent heat effect proves to be a destabilizing influence. As in the case of the olivine–spinel phase change,  $R_{\beta_{crit}}$  is generally insensitive to  $|R_Q|$ , until  $|R_Q|$  reaches sufficiently large values dependent on  $|S|$ . In all, one can conclude that the spinel–post-spinel transition appears to be rather unstable. A finite amplitude calculation of convection through this phase change (Richter 1973b) at  $R_{\beta} = 125$ ,  $R_Q = -60$ , and  $S = -0.15$  confirms that it does not act as a barrier to vertical motions. According to the linear stability curve of Fig. 4, convection would occur through the 650-km phase change at the above values of  $R_Q$  and  $S$  for  $R_{\beta}$  an order of magnitude smaller than considered in the numerical finite-amplitude example.

The endothermic spinel–post-spinel phase transformation cannot be the ‘mechanical brake’ to convection invoked by Kumazawa *et al.* (1974) and Jackson, Liebermann & Ringwood (1974). The idea of partition differentiation of Fe and Mg between the lower and upper mantle through a horizon at about 700 km depth (Garlick 1969; Kumazawa *et al.* 1974) is to be questioned if convection can penetrate the phase change. The feasibility of convection through the 650-km discontinuity also calls to question the Mereu, Simpson & King (1974) interpretation, based on  $Q$  contrasts for body waves, of a return convective flow at this depth.

Even on the basis of an extensive set of normal mode data (Anderssen & Cleary 1974; Gilbert & Dziewonski 1975) and a new shear wave velocity model for the upper 1200 km of the mantle from waveforms and travel times (Helmberger & Engen 1974), it is presently not possible to adequately resolve the fine structure of the density and the seismic velocities in the region of the two seismic discontinuities, where the

**Table 2***Parameters for the stability analysis of the univariant spinel–oxide transformation*

$2 \times 10^{-5} \text{ } ^\circ\text{K}^{-1} \lesssim \alpha \lesssim 2.5 \times 10^{-5} \text{ } ^\circ\text{K}^{-1}$	Jacobs (1956), Ito, Kawada & Akimoto (1974)
$0.08 \lesssim \Delta\rho/\rho \lesssim 0.10$	Ahrens & Syono (1967), Anderson (1967), Davies (1974)
$-20b \text{ } ^\circ\text{K}^{-1} \lesssim \gamma \lesssim -10b \text{ } ^\circ\text{K}^{-1}$	Ahrens & Syono (1967), Bassett & Ming (1972)
$2300 \text{ } ^\circ\text{K} \lesssim T \lesssim 2400 \text{ } ^\circ\text{K}$	Schubert <i>et al.</i> (1969)
$10^{23} \text{ cm}^2 \text{ s}^{-1} \lesssim \nu \lesssim 10^{26} \text{ cm}^2 \text{ s}^{-1}$	McKenzie (1967), Stocker & Ashby (1973), Cathles (1971), Brennen (1974)
$10^{-2} \text{ cm}^2 \text{ s}^{-1} \lesssim \kappa \lesssim 2 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$	Schatz & Simmons (1972)
$600 \text{ km} \lesssim D \lesssim 700 \text{ km}$	Archambeau <i>et al.</i> (1969), Wiggins & Helmberger (1973), Massé (1974)
$1 \text{ } ^\circ\text{K km}^{-1} \lesssim \beta \lesssim 5 \text{ } ^\circ\text{K/km}$	Schubert <i>et al.</i> (1969)
$c_p \approx 1.25 \times 10^7 \text{ erg g}^{-1} \text{ } ^\circ\text{K}^{-1}$	Jacobs (1956)
$-0.4 \lesssim S \lesssim -0.1$	
$-700 \lesssim R_Q \lesssim -0.04$	

phase changes are presumed to take place. We cannot yet distinguish, seismologically, a static from a dynamic equilibrium between the upper and the lower mantle; a possible consequence of the former is a chemically layered mantle, whose profound stabilizing influence on convection has been emphasized by Richter & Johnson (1974). In this connection, separate convection cells could exist within each chemically homogeneous region of the mantle. Recent work on the relationship between acoustic velocity and mean atomic weight (Liebermann 1973; Liebermann & Ringwood 1973; Davies 1974; Wang & Simmons 1972) has shown that the iron enrichment of the lower mantle (Anderson & Jordan 1970) may have been an overestimate. The overall olivine-spinel-oxides transition could thus occur at uniform composition.

### Stability of a divariant phase transformation

In the previous section on phase transitions and their effects on mantle dynamics, a single component, or univariant system was treated. However, from mineralogical and geochemical data the Earth is actually a polyvariant system with many components coexisting at the same pressure and temperature. We present here the first quantitative treatment of the stability of a fluid layer with a divariant phase transition. As part of the theory, we develop the necessary thermodynamic formalism for the divariant system.

From equilibrium thermodynamics one can invoke the Gibbs phase rule for non-reacting chemical species to obtain the number of thermodynamic degrees of freedom  $F$  for a given physical-chemical system:  $F = C - P + 2$ , where  $C$  is the number of components in the ensemble, and  $P$  is the number of co-existing phases. Therefore, a univariant system undergoing a phase change has one degree of thermodynamic freedom, namely the Clapeyron or equilibrium curve which relates pressure  $p$  and temperature  $T$  in a unique manner. For a divariant system undergoing a phase transition, there is an additional degree of freedom and within the divariant two-phase region there is a no *a priori* relationship between  $T$  and  $p$ . We proceed to establish the thermodynamic formalism required for the stability analysis of a layer of fluid with a divariant phase change. The theory is valid for any such phase transformation, however, for clarity in discussion and simplicity of notation we use the olivine-spinel transition as the representative phase change.

#### Basic state

For the binary system of  $\text{Mg}_2\text{SiO}_4$ , forsterite, and  $\text{Fe}_2\text{SiO}_4$ , fayalite, the thermodynamic variables  $T$ ,  $p$ , and  $\chi$ , the mole fraction of forsterite, provide a complete description of the system. From the experimentally determined phase diagrams (Ringwood & Major 1966, 1970; Akimoto & Fujisawa 1968; Ahrens 1973) one can construct the two implicit functions  $F_U(T, p, \chi) = 0$  and  $F_L(T, p, \chi) = 0$  which represent the upper and lower surfaces of the divariant two-phase region, as sketched in Fig. 6. For simplicity, we do not distinguish between the  $\gamma$  and  $\beta$ -phases, which have nearly the same free energies (Ringwood & Major 1970). The overall composition of the system  $\chi = \chi_0$  is a constant. Since  $F = 2$ , within the two-phase region the system can exist in equilibrium at any  $T$ ,  $p$  point in the  $\chi_0$  plane lying between the surfaces  $F_U = 0$  and  $F_L = 0$ , in contrast to the univariant case where there is a definite relationship, the Clapeyron curve, between  $T$  and  $p$ .

In the motionless state, we suppose that the two-phase region extends from a depth  $D-d$  to the depth  $D+d$  (this notation is convenient for the stability analysis to follow). The depth to the centre of the transition zone  $D$  and the thickness of the region  $2d$  are determined as follows. From the definitions of  $F_U$  and  $F_L$ , we have

$$F_U\{T(D+d), p(D+d), \chi_0\} = 0, \quad (6)$$

$$F_L\{T(D-d), p(D-d), \chi_0\} = 0, \quad (7)$$

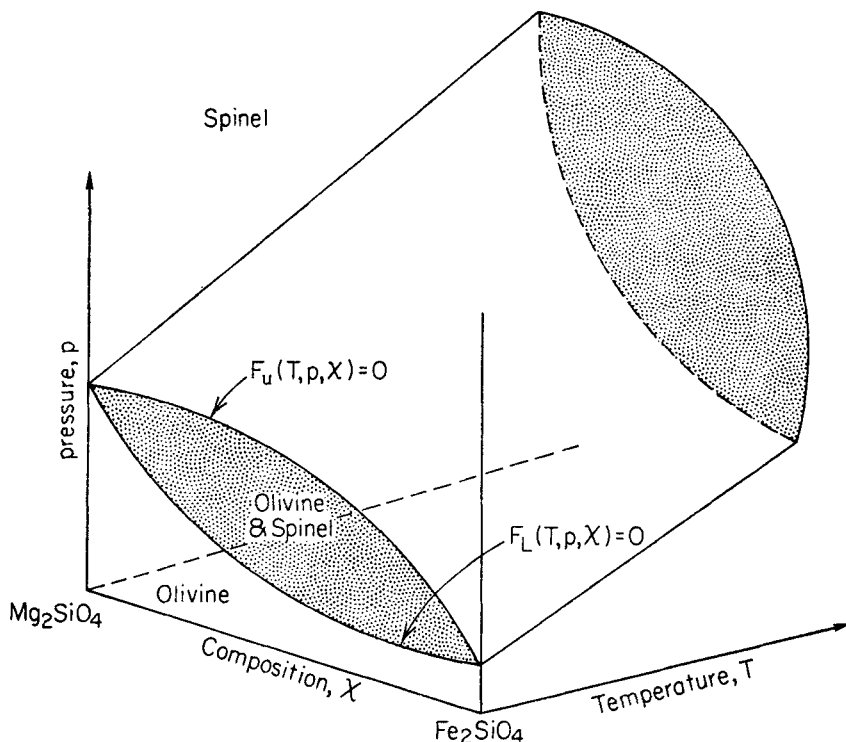


FIG. 6. Schematic phase diagram of the  $Mg_2SiO_4$ - $Fe_2SiO_4$  binary system in pressure  $p$ , temperature  $T$  and composition  $\chi$  space.  $F_u(T, p, \chi) = 0$  and  $F_L(T, p, \chi) = 0$  are the surfaces separating the two-phase region from the pure phase regions.

The hydrostatic variation of pressure with depth leads to

$$p(D-d) = g \int_{\text{surface}}^{D-d} \rho^{ol} dz, \tag{8}$$

where  $\rho^{ol}$  is the density of olivine, and

$$p(D+d) = p(D-d) + g \int_{D-d}^{D+d} \bar{\rho} dz, \tag{9}$$

where  $\bar{\rho}$  is the density in the two-phase region (henceforth an overbar will denote a property of the transition zone between single phases).

Equations (6)–(9) suffice to determine  $D$  and  $d$  if the temperature is known as a function of depth (the conduction temperature profile is assumed, as appropriate to the basic state of a stability analysis) and we understand how to evaluate the density.

In terms of the forsterite mole fraction  $\chi_0$ , the density of olivine can be written

$$\rho^{ol} = \frac{\rho_{fo}^{ol} \chi_0 + \rho_{fa}^{ol} (1 - \chi_0) \frac{\rho_{fo}^{ol}}{\rho_{fa}^{ol}} \frac{MW_{fa}}{MW_{fo}}}{\frac{\rho_{fo}^{ol}}{\rho_{fa}^{ol}} \frac{MW_{fa}}{MW_{fo}} (1 - \chi_0) + \chi_0}, \tag{10}$$

where  $\rho_{fo}^{ol}$  and  $\rho_{fa}^{ol}$  are the densities of pure forsterite and pure fayalite in the olivine phase, respectively, and  $MW_{fo}$  and  $MW_{fa}$  are the molecular weights of forsterite and fayalite. Although  $\rho_{fa}^{ol}$  and  $\rho_{fo}^{ol}$  are different by as much as 30–40 per cent, the molar volumes of forsterite and fayalite in olivine are nearly the same, i.e.

$$\frac{\rho_{fo}^{ol}}{\rho_{fa}^{ol}} \frac{MW_{fa}}{MW_{fo}} \approx 1$$

(Chung 1971), so that we may approximate  $\rho^{ol}$  by

$$\rho^{ol} \approx \rho_{fo}^{ol}\chi_0 + \rho_{fa}^{ol}(1-\chi_0). \quad (11)$$

A similar result holds for the density of spinel  $\rho^{sp}$ ,

$$\rho^{sp} \approx \rho_{fo}^{sp}\chi_0 + \rho_{fa}^{sp}(1-\chi_0). \quad (12)$$

The densities of olivine and spinel as a function of Fe/Mg ratio, temperature and pressure are given by Chung (1971, 1972).

To describe the density in the two-phase region, we must use the lever-rule (Ehlers 1972) to determine the compositions of the olivine and spinel phases which vary

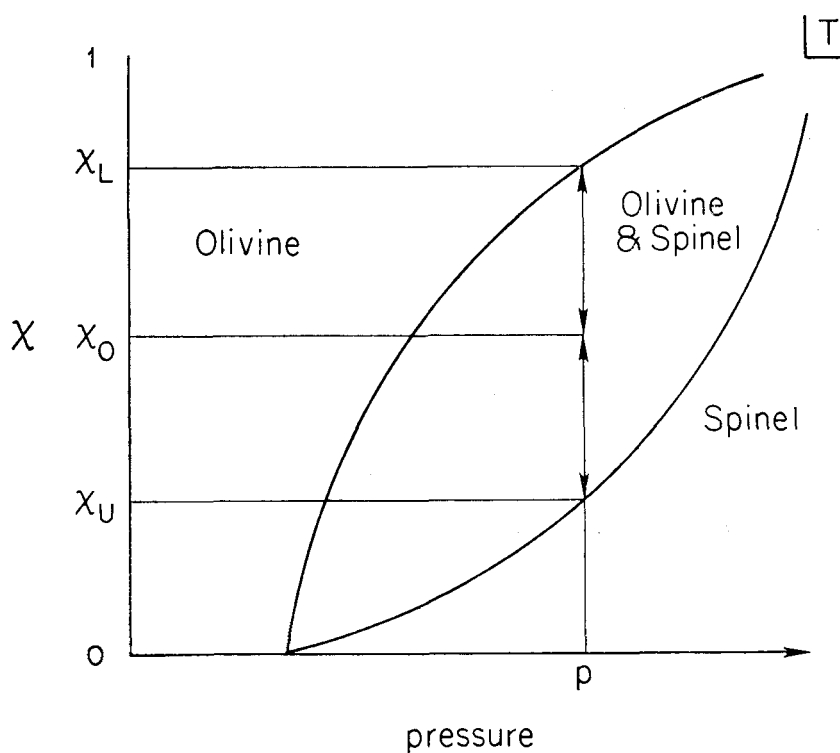


FIG. 7. An isothermal cross-section of the three-dimensional phase diagram in Fig. 6 illustrating the principle of the lever rule.  $\chi_0$  is the mole fraction of forsterite in the pure olivine or spinel phases.  $\chi_L$  and  $\chi_U$  are determined at a particular value of  $p$  according to the figure. The scale for  $\chi$  ranges from 0 (pure  $\text{Fe}_2\text{SiO}_4$ ) to 1 (pure  $\text{Mg}_2\text{SiO}_4$ ).

through the transition zone. The situation is sketched in Fig. 7, from which we find

$$\begin{aligned}
 x^{sp} &= \text{mole fraction of spinel in two-phase region} \\
 &= \frac{\chi_L(T, p) - \chi_0}{\chi_L(T, p) - \chi_U(T, p)}, \tag{13}
 \end{aligned}$$

$$\begin{aligned}
 x^{ol} &= \text{mole fraction of olivine in two-phase region} \\
 &= \frac{\chi_0 - \chi_U(T, p)}{\chi_L(T, p) - \chi_U(T, p)}, \tag{14}
 \end{aligned}$$

where  $\chi_U(T, p)$  is the mole fraction (molar composition in per cent) of forsterite in the spinel component of the two-phase system and  $\chi_L(T, p)$  is the mole fraction of forsterite in the olivine member of the two-phase system. The overall mole fraction of forsterite for both phases is  $\chi_0$ .

The molar weight of the two-phase assemblage is

$$MW_{fo}(x^{ol} \chi_L + x^{sp} \chi_U) + MW_{fa}(x^{ol}(1 - \chi_L) + x^{sp}(1 - \chi_U)).$$

Assuming ideal solution behaviour, i.e. that the volumes of the components are additive, we find that the molar volume of the two-phase system is

$$\frac{MW_{fo}}{\rho_{fo}^{ol}} x^{ol} \chi_L + \frac{MW_{fo}}{\rho_{fo}^{sp}} x^{sp} \chi_U + \frac{MW_{fa}}{\rho_{fa}^{ol}} x^{ol}(1 - \chi_L) + \frac{MW_{fa}}{\rho_{fa}^{sp}} x^{sp}(1 - \chi_U).$$

The density of the two-phase assemblage  $\bar{\rho}$  is the ratio of the molar weight to the molar volume, a quantity which may be approximately written as

$$\bar{\rho} \approx x^{ol} \chi_L \rho_{fo}^{ol} + x^{ol}(1 - \chi_L) \rho_{fa}^{ol} + x^{sp} \chi_U \rho_{fo}^{sp} + x^{sp}(1 - \chi_U) \rho_{fa}^{sp}. \tag{15}$$

This simplified expression for  $\bar{\rho}$  requires

$$\frac{MW_{fa}}{MW_{fo}} \frac{\rho_{fo}^{ol}}{\rho_{fa}^{ol}} \approx 1, \quad \frac{MW_{fa}}{MW_{fo}} \frac{\rho_{fo}^{sp}}{\rho_{fa}^{sp}} \approx 1, \quad \frac{\rho_{fo}^{ol}}{\rho_{fo}^{sp}} \approx 1,$$

approximations which are valid according to the density values reported by Chung (1971, 1972).

From the curvatures of the phase space surfaces  $F_U = 0$  and  $F_L = 0$ , we can evaluate the expressions  $(\partial x^{ol}/\partial p)_T$  and  $(\partial x^{ol}/\partial T)_p$  which we will need shortly in our derivations of the effective coefficient of thermal expansion, specific heat and adiabatic gradient in the two-phase divariant region. Differentiating (14) we find

$$\left( \frac{\partial x^{ol}}{\partial p} \right)_T = \frac{(\chi_U - \chi_0)(\partial \chi_L/\partial p)_T + (\chi_0 - \chi_L)(\partial \chi_U/\partial p)_T}{(\chi_L - \chi_U)^2}, \tag{16}$$

$$\left( \frac{\partial x^{ol}}{\partial T} \right)_p = \frac{(\chi_U - \chi_0)(\partial \chi_L/\partial T)_p + (\chi_0 - \chi_L)(\partial \chi_U/\partial T)_p}{(\chi_L - \chi_U)^2}, \tag{17}$$

which, if we approximate

$$\left( \frac{\partial \chi_L}{\partial p} \right)_T \approx \left( \frac{\partial \chi_U}{\partial p} \right)_T \quad \text{and} \quad \left( \frac{\partial \chi_L}{\partial T} \right)_p \approx \left( \frac{\partial \chi_U}{\partial T} \right)_p,$$

can be written

$$\left(\frac{\partial x^{ol}}{\partial p}\right)_T = -\frac{(\partial\chi_L/\partial p)_T}{(\chi_L - \chi_U)}, \quad (18)$$

$$\left(\frac{\partial x^{ol}}{\partial T}\right)_p = -\frac{(\partial\chi_L/\partial T)_p}{(\chi_L - \chi_U)}. \quad (19)$$

From the phase diagrams of the olivine–spinel transition we find that (18) and (19) can be used for values of  $\chi_0$  of geophysical interest, i.e.  $\chi_0$  between 0.85 and 0.90. According to Le Châtelier's principle  $(\partial x^{ol}/\partial p)_T$  and  $(\partial x^{ol}/\partial T)_p$  should be negative and positive quantities, respectively. These signs are in agreement with those implied by (18) and (19).

*Adiabatic gradient, specific heat and coefficient of expansion in the two-phase divariant region*

For simplicity in what follows we will ignore the variations in composition of the olivine and spinel components in the two-phase divariant region, i.e. the properties of olivine and spinel will be evaluated at the composition  $\chi_0$  of the overall system. For example, in the expression for the density in the two-phase divariant region (15) we assume  $\chi_U \approx \chi_L \approx \chi_0$  and derive

$$\bar{\rho} \approx x^{ol} \rho^{ol} + (1 - x^{ol}) \rho^{sp}, \quad (20)$$

where  $\rho^{ol}$  and  $\rho^{sp}$  are given by (11) and (12). Expression (20) is an excellent approximation to  $\bar{\rho}$  throughout the two-phase divariant region of the olivine–spinel transition.

We can see from (20) that perturbations in density in the two-phase region will arise from changes in  $\rho^{ol}$  and  $\rho^{sp}$  induced primarily by temperature fluctuations and from changes in  $x^{ol}$  also mainly due to temperature variations. Differentiating (20) we find

$$\delta\bar{\rho} = x^{ol}(\delta\rho^{ol} - \delta\rho^{sp}) + \delta\rho^{sp} + \delta x^{ol}(\rho^{ol} - \rho^{sp}). \quad (21)$$

Neglecting effects of compressibility on the individual phases, we write

$$\delta\rho^{ol} \approx -\rho^{ol} \alpha \delta T, \quad (22)$$

$$\delta\rho^{sp} \approx -\rho^{sp} \alpha \delta T, \quad (23)$$

where  $\delta T$  is the temperature perturbation and we have assumed that both phases have the same ordinary coefficient of thermal expansion  $\alpha$ . Using (22) and (23) in (21) we find

$$\frac{\delta\bar{\rho}}{\bar{\rho}} = -\alpha \delta T - \frac{\Delta\rho}{\bar{\rho}} \delta x^{ol}, \quad (24)$$

where, as before  $\Delta\rho \equiv \rho^{sp} - \rho^{ol}$ .

Perturbations in the olivine mole fraction  $\delta x^{ol}$  are related to temperature and pressure perturbations by

$$\delta x^{ol} = \left(\frac{\partial x^{ol}}{\partial p}\right)_T \delta p + \left(\frac{\partial x^{ol}}{\partial T}\right)_p \delta T. \quad (25)$$

Using (18) and (19) and the empirical phase diagrams for the olivine–spinel transition, we find that  $\delta x^{ol}$  is due mainly to temperature perturbations, so that

$$\frac{\delta\bar{\rho}}{\bar{\rho}} = -\delta T \left( \alpha + \frac{\Delta\rho}{\bar{\rho}} \left(\frac{\partial x^{ol}}{\partial T}\right)_p \right). \quad (26)$$



From (26) we can define an effective coefficient of thermal expansion for the two-phase divariant region

$$\bar{\alpha} \equiv \alpha + \frac{\Delta\rho}{\bar{\rho}} \left( \frac{\partial x^{ol}}{\partial T} \right)_p \tag{27}$$

For the olivine–spinel system and for  $x_0 \approx 0.85$  we calculate that the phase change contribution to thermal expansion in the two-phase region (the second term on the right-hand side of (27)) is  $0(10^{-4}$  to  $10^{-3} \text{ K}^{-1})$ , one to two orders of magnitude larger than ordinary thermal expansivity  $\alpha$ .

Liberation and absorption of latent heat in the two-phase region can be accounted for by the introduction of an effective specific heat  $\bar{c}_p$ . From the definition of specific heat at constant pressure

$$\bar{c}_p = T \left( \frac{\partial \bar{s}}{\partial T} \right)_p \tag{28}$$

and

$$\bar{s} = x^{ol} s^{ol} + (1 - x^{ol}) s^{sp}, \tag{29}$$

where  $s^{ol}$  and  $s^{sp}$  are evaluated at the composition  $x_0$ , we find

$$\bar{c}_p = c_p + \left( \frac{\partial x^{ol}}{\partial T} \right)_p T (s^{ol} - s^{sp}). \tag{30}$$

In obtaining (30) we have assumed that the ordinary specific heat  $c_p$  of the individual phases are identical. We will suppose, for simplicity, that  $\bar{c}_p$  is a constant in the two-phase region.

From (30) it is clear that the heat capacity at constant pressure has been increased in the two-phase divariant region. The same result holds for a heat-absorbing phase change, such as the spinel-oxide transition, since Le Châtelier’s principle dictates that an increase in temperature would drive the two-phase system to the denser phase. The phase change contribution to  $\bar{c}_p$  is at best of the same order of magnitude as the single-phase specific heat  $c_p$ . Another consequence of the increase in  $\bar{c}_p$  would be the decrease in  $\bar{\kappa}$  the thermal diffusivity in the two-phase divariant region.

For a single component system, the magnitude of the adiabatic temperature gradient  $\beta_a$  is

$$\beta_a = \left( \frac{\partial \rho^{-1}}{\partial T} \right)_p \left( \frac{g\rho T}{c_p} \right). \tag{31}$$

In the two-phase divariant region, the adiabatic temperature gradient  $\bar{\beta}_a$  can be derived by differentiation of expression (29) for entropy

$$\begin{aligned} \delta\bar{s} = \delta T \left\{ \Delta s \left( \frac{\partial x^{ol}}{\partial T} \right)_p + \left( \frac{\partial s^{sp}}{\partial T} \right)_p + x^{ol} \left( \left( \frac{\partial s^{ol}}{\partial T} \right)_p - \left( \frac{\partial s^{sp}}{\partial T} \right)_p \right) \right\} \\ + \delta p \left\{ \Delta s \left( \frac{\partial x^{ol}}{\partial p} \right)_T + \left( \frac{\partial s^{sp}}{\partial p} \right)_T + x^{ol} \left( \left( \frac{\partial s^{ol}}{\partial p} \right)_T - \left( \frac{\partial s^{sp}}{\partial p} \right)_T \right) \right\}, \tag{32} \end{aligned}$$

where  $\Delta s = s^{ol} - s^{sp}$ . By setting  $\delta\bar{s}$  equal to zero in (32) and substituting  $\delta p = -\bar{\rho}g\delta z$ , we can determine the ratio of  $\delta T$  and  $\delta z$  at constant entropy, so that

$$\bar{\beta}_a = \frac{\alpha g T - \bar{\rho} g T \Delta s (\partial x^{ol} / \partial p)_T}{c_p + T \Delta s (\partial x^{ol} / \partial T)_p}. \tag{33}$$

In obtaining (33) we employed the Maxwell relations for the individual phases and assumed that the ordinary thermal expansivity and specific heat at constant pressure were identical for each of the pure phases. For simplicity in determining the stability of the divariant phase change we treat  $\beta_a$  as a constant in the analysis of the next section.

Ringwood's (1972) formula,  $(\Delta\rho gT)/(\rho Q)$ , for the magnitude of the effective adiabatic temperature gradient in a multi-component system is only an estimate provided by the ratio of the second terms in the numerator and denominator of (33). With  $(\partial x^{ol}/\partial T)_p \approx 10^{-3}$  to  $10^{-2} \text{ }^\circ\text{K}^{-1}$ ,  $-(\partial x^{ol}/\partial p)_T \approx 10^{-2}$  to  $10^{-1} \text{ kbar}^{-1}$ ,  $T\Delta s \approx 40 \text{ cal g}^{-1}$ ,  $\alpha \approx 3 \times 10^{-5} \text{ }^\circ\text{K}^{-1}$ ,  $g = 10^3 \text{ cm s}^{-2}$ ,  $T \approx 2000 \text{ }^\circ\text{K}$ ,  $c_p \approx 0.3 \text{ cal g}^{-1} \text{ }^\circ\text{K}^{-1}$ ,  $\bar{\rho} \approx 3.6 \text{ g cm}^{-3}$ , we find  $\bar{\beta}_a = 1$  to  $2 \text{ }^\circ\text{K km}^{-1}$ , smaller than Ringwood's (1972) estimate of 4 to  $5 \text{ }^\circ\text{K km}^{-1}$ . In our model of the olivine-spinel transition, the adiabatic gradient is discontinuous at the two interfaces which bound the divariant two-phase region.

#### Divariant phase change stability analysis

Consider the stability of the olivine-spinel layer shown in Fig. 8. The two-phase divariant region occupies  $-d \leq z \leq d$ , olivine lies between  $z = d$  and  $z = D$ ,  $D > d$ , and spinel is the phase between  $z = -d$  and  $z = -D$ . The properties  $\alpha$ ,  $\kappa$ ,  $\nu$ ,  $\rho$ ,  $\beta_a$ ,  $\bar{\alpha}$  and  $\bar{\beta}_a$  are treated as constants; from among the various properties of the system

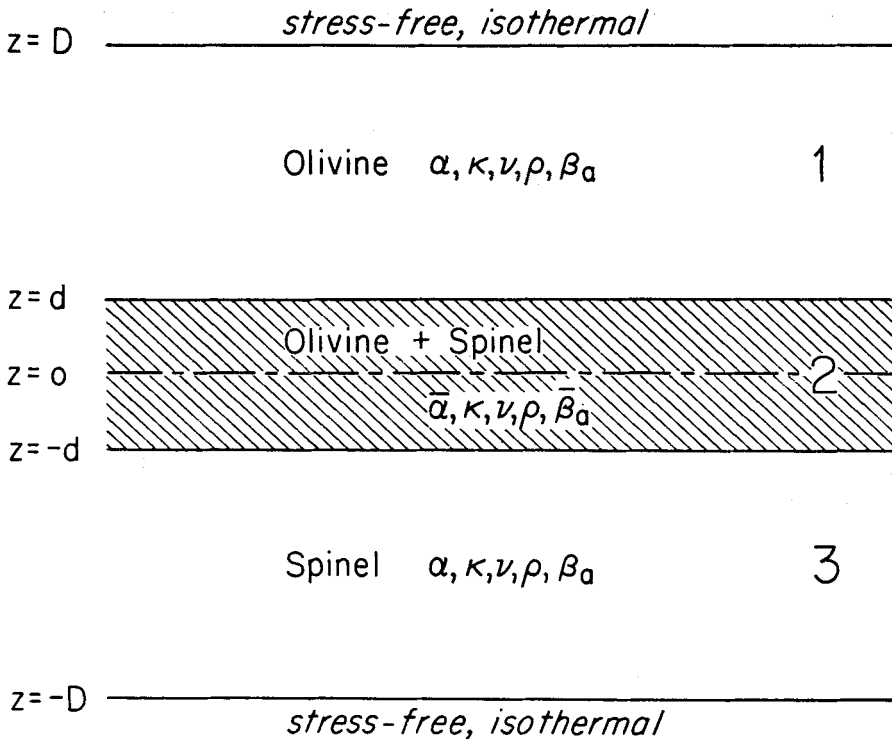


FIG. 8. Divariant olivine-spinel layer of thickness  $2D$  with a centred two-phase region of width  $2d$ . The physical parameters are everywhere the same, except in the two-phase zone where the effective coefficient of thermal expansion  $\bar{\alpha}$  and the adiabatic temperature gradient  $\bar{\beta}_a$  are different from  $\alpha$  and  $\beta_a$  in the pure phase regions. The stress-free and isothermal notations refer to the boundary conditions applied in the divariant phase change stability analysis.

only the effective coefficient of thermal expansion  $\bar{\alpha}$  and the adiabatic gradient  $\bar{\beta}_a$  in the two-phase zone are distinguished from their counterparts in the single-phase regions. We neglect the possible differences in the other properties between the two-phase and single-phase regions and between the pure olivine and spinel phases. It is conceivable that significant changes in thermodynamic or rheological properties, not included here, might accompany the mineralogical phase changes in the Earth. For example, Sammis & Dein (1974) have recently discussed the phenomenon of superplasticity in phase transition zones from experimental observations of the  $\beta$ - $\alpha$  transformation in *CsCl* at 733°K. We must regard such a change in the rheological behaviour of olivine-spinel as potentially important but presently rather speculative. In the undisturbed state there is a constant negative temperature gradient of absolute magnitude  $\beta$  and a pressure gradient  $-\rho g$  throughout the fluid layer. The static state is, of course, horizontally homogeneous. The subscripts 1, 2 and 3 refer to the olivine, olivine-spinel, and spinel regions, respectively.

The linearized equations for the velocity perturbations  $\mathbf{u}$ , the temperature perturbations  $\theta$  and the pressure perturbations  $\pi$  are

$$\nabla \cdot \mathbf{u}_{1, 2, 3} = 0 \tag{34}$$

(we assume each region can be treated as a Boussinesq fluid layer),

$$-\frac{1}{\rho} \nabla \pi_{1, 2, 3} + v \nabla^2 \mathbf{u}_{1, 2, 3} + g \hat{\mathbf{z}} \begin{pmatrix} \alpha \theta_{1, 3} \\ \bar{\alpha} \theta_2 \end{pmatrix} = 0, \tag{35}$$

$$-\kappa \nabla^2 \theta_{1, 2, 3} = \begin{pmatrix} (\beta - \beta_a) w_{1, 3} \\ (\beta - \bar{\beta}_a) w_2 \end{pmatrix}, \tag{36}$$

where  $w$  is the vertical component of the perturbation velocity and  $\hat{\mathbf{z}}$  is a unit vector in the positive  $z$ -direction. We have assumed that the state of marginal stability is given by  $(\partial)/(\partial t) = 0$ , i.e. that the principle of exchange of stabilities is valid.

The boundary conditions at  $z = \pm D$  are  $w = \theta = (\partial^2 w)/(\partial z^2) = 0$ , i.e. these boundaries are stress-free, isothermal ones. At the interfaces between the single-phase and two-phase regions,  $z = \pm d$ ,  $w$ ,  $(\partial w)/(\partial z)$ ,  $(\partial^2 w)/(\partial z^2)$ ,  $\pi$ ,  $\theta$  and  $(\partial \theta)/(\partial z)$  are all continuous. This contrasts with the univariant case where the perturbation temperature gradient and perturbation pressure are discontinuous at the phase change interface. Thus, in the linearized treatment of the divariant phase change stability there is no distortion of the phase boundaries at the onset of instability; the density change and latent heat release are directly incorporated into the momentum and energy equations through  $\bar{\alpha}$  and  $\bar{\beta}_a$  instead of via the boundary conditions on perturbation heat flux and pressure as in the univariant phase change stability theory. When the motions reach finite amplitude, the two-phase divariant region will, of course, be displaced from its equilibrium (motionless) position in a manner similar to that of the univariant phase change interface.

Without loss of generality, we consider the two-dimensional periodic solutions of (34)–(36) with horizontal wave number  $l$ . The symmetric solutions for the vertical velocity and temperature perturbations in regions 1 and 3 are

$$w_{1, 3} = \sum_{n=1}^3 A_n \sinh \delta_n (1 \pm z/D), \tag{37}$$

$$\theta_{1, 3} = \sum_{n=1}^3 A_n v \frac{(\delta_n^2 - l^2 D^2)^2}{\alpha g D^2 (l^2 D^2)} \sinh \delta_n (1 \pm z/D), \tag{38}$$

where

$$\left. \begin{aligned} \delta_n^2 &= l^2 D^2 + (R_\beta l^2 D^2)^\dagger \exp(i(\pi/3)(2n-1)), \\ n &= 1, 2, 3. \end{aligned} \right\} \quad (39)$$

$A_n$  are constants of integration and the upper and lower signs on the right-hand sides of (37) and (38) refer to regions 3 and 1, respectively. Equations (37) and (38) provide solutions for  $w$  and  $\theta$  which automatically satisfy the boundary conditions on  $z = \pm D$ .

The symmetric solution for the two-phase divariant region is

$$w_2 = \sum_{n=1}^3 B_n \cosh \delta_n(z/D), \quad (40)$$

$$\theta_2 = \sum_{n=1}^3 B_n \frac{v(\delta_n^2 - l^2 D^2)^2}{\bar{\alpha} g D^2 (l^2 D^2)} \cosh \delta_n(z/D), \quad (41)$$

where

$$\left. \begin{aligned} \delta_n^2 &= l^2 D^2 + \{((\bar{\alpha}/\alpha)R_\beta - R)l^2 D^2\}^\dagger \exp(i(\pi/3)(2n-1)), \\ n &= 1, 2, 3. \end{aligned} \right\} \quad (42)$$

and

$$R = \frac{\bar{\alpha}(\bar{\beta}_a - \beta_a)gD^4}{\kappa v}. \quad (43)$$

The boundary conditions at either  $z = d$  or  $z = -d$  provide six equations for the six unknowns  $A_n$  and  $B_n$ . These equations are homogeneous and by setting their  $6 \times 6$  coefficient determinant equal to zero we arrive at an eigenvalue equation for the Rayleigh number  $R_\beta$ .

The parameter  $R$  has the form of a Rayleigh number based on the amount by which the two-phase adiabatic temperature gradient exceeds that of the single phase region. For the olivine-spinel transformation,  $\bar{\beta}_a > \beta_a$  and  $R$  is positive. The increased stabilizing influence of the adiabatic temperature gradient in the two-phase region was noted by Ringwood (1972). We can quantitatively assess the importance of the stabilizing influence of the increased adiabatic gradient in the two-phase region by determining the dependence of Rayleigh number on  $R$ . Thus we will be concerned with the situation in which the basic temperature gradient  $\beta$  exceeds the adiabatic temperature gradient in the single-phase regions,  $\beta > \beta_a$ , but is less than the adiabatic temperature gradient in the two-phase zone  $\beta < \bar{\beta}_a$ . We also consider the case where  $\beta > \bar{\beta}_a > \beta_a$ .

The Rayleigh number is a function of the following parameters

$$R_\beta = R_\beta(lD, d/D, \bar{\alpha}/\alpha, R). \quad (44)$$

A minimum, critical Rayleigh number  $R_{\beta_{\text{crit}}}$  exists for a certain value of  $lD$  which depends upon the other dimensionless parameters  $d/D$ ,  $\bar{\alpha}/\alpha$  and  $R$ ; we will henceforth only be interested in

$$R_{\beta_{\text{crit}}} = R_{\beta_{\text{crit}}}(d/D, \bar{\alpha}/\alpha, R). \quad (45)$$

The divariant two-phase olivine-spinel region provides a destabilizing influence to compete with the stabilizing one associated with the increased adiabatic gradient. This destabilizing effect enters through the parameter  $\bar{\alpha}/\alpha$ . Since the effective coefficient of thermal expansion is significantly larger in the two-phase olivine-spinel region, the buoyancy force driving convective instability is enhanced in this transition zone. Thus, by increasing  $d/D$ , the fractional width of the transition zone, buoyancy

can be enhanced throughout the fluid layer leading to a greater degree of instability. The overall effect of the phase change on stability of the fluid layer, as compared with the stability of a single phase fluid, requires quantitative evaluation of  $R_{\beta_{\text{crit}}}$ .

Richter's (1973a, b) finite amplitude calculations of convection through a univariant phase change included a finite width two-phase region centred about the intersection of the temperature-depth curve with the Clapeyron curve. In this way, both the mole-fraction distribution of olivine,  $x^{\text{ol}}$ , in the two-phase region and the thickness of the region were structured beforehand. A more realistic finite amplitude approach would be to incorporate the divariant nature of the olivine-spinel phase change by employing the three-dimensional phase diagrams for this system. In this way, both the olivine mole-fraction structure in the two-phase region, the width of the region, and the distortions of the phase change interfaces can be properly accounted for.

Our discussion of the stability of a divariant phase change has centred on the olivine-spinel transition as the prime example. Before proceeding further, it is worthwhile considering the spinel-post-spinel transformation. The spinel-oxide transition provides an interesting contrast to the olivine-spinel transformation, in that  $\bar{\alpha}/\alpha$  is less than unity and may even be negative in the former case. This can be seen physically by noting from Le Châtelier's principle that the addition of heat to the spinel-oxide system would tend to evolve more of the oxide phase leading to an effective thermal expansivity smaller than the ordinary  $\alpha$  and perhaps even negative. Also, the adiabatic temperature gradient in the spinel-oxide transition zone would be reduced as compared with the ordinary  $\beta_a$ .

This is easily understood by considering the effect of adiabatically pressurizing a parcel of spinel. Upon transforming to the oxides heat would be absorbed thus tending to reduce the temperature rise with compression. Thus, from the divariant point of view, there are also two competing effects governing the stability of the spinel-oxide transition, however, the roles of  $\bar{\alpha}/\alpha$  and  $\beta_a$  are reversed from the olivine-spinel transformation.

#### *Critical Rayleigh number for the divariant olivine-spinel phase change*

We first examine the tendency of the phase change itself to drive convection in the whole fluid layer by neglecting buoyancy in the single-phase regions, i.e. we take  $\alpha$ , the ordinary thermal expansion coefficient, equal to zero. Consequently, the adiabatic gradient in the pure olivine and spinel regions is also zero. The problem reduces to the stability of a fluid layer within which buoyancy forces are confined to a centred fraction  $d/D$  of the layer, the remainder of the fluid being passive. The eigenvalue parameter for this problem is a Rayleigh number of the form

$$\bar{R}_{\beta} = \frac{\bar{\alpha}gD^4(\beta - \beta_a)}{\kappa\nu}, \quad (46)$$

the minimum critical value of which  $\bar{R}_{\beta_{\text{crit}}}$  depends only on  $d/D$ .

Fig. 9 shows  $\bar{R}_{\beta_{\text{crit}}}$  as a function of  $d/D$ . For  $d/D = 1$ ,  $\bar{R}_{\beta_{\text{crit}}}$  corresponds to  $R_{\beta_{\text{crit}}}^*$  for the ordinary Rayleigh-Bénard problem since the buoyant region occupies the entire fluid layer. As  $d/D$  decreases and less of the layer is buoyant, the critical Rayleigh number increases, but very slowly until  $d/D$  becomes less than about 0.1. The onset of convection in the fluid layer is relatively insensitive to the reduction of buoyancy in a large portion of the layer. Of course, the stability of the whole system strongly increases as  $d/D$  is further reduced below 0.1. As  $d/D$  approaches zero, the critical Rayleigh number from this analysis would tend to infinity. However, with  $d/D \rightarrow 0$  the problem would approach that of the univariant phase boundary separating two pure phases neither of which have ordinary thermal expansivity. This

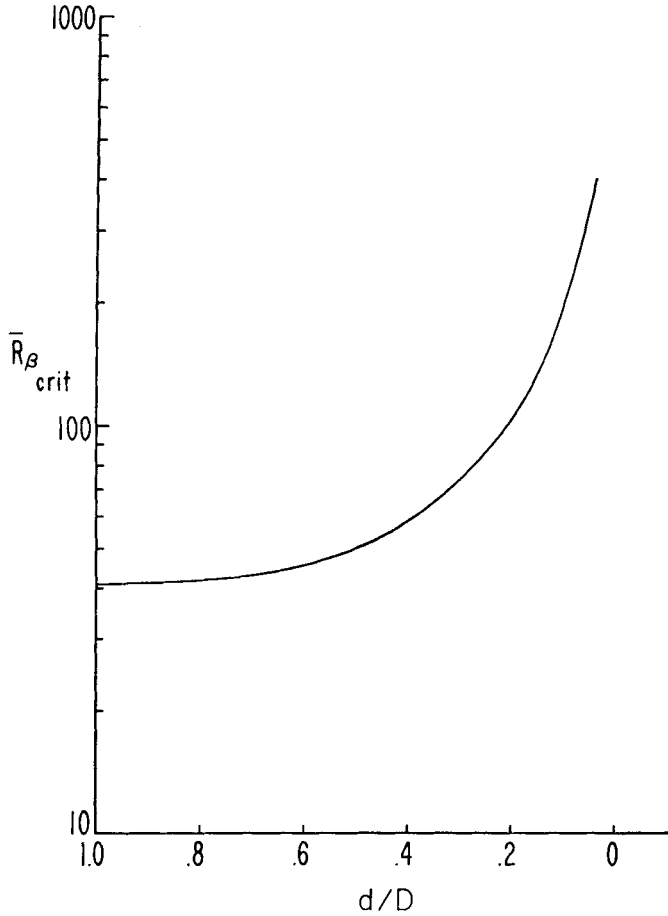


FIG. 9. The critical Rayleigh number  $\bar{R}_{\beta_{crit}}$  for the onset of instability in a fluid layer of thickness  $2D$  with a divariant two-phase region of width  $2d$ . The layer is bouyant only in the phase transition zone, i.e. the ordinary thermal expansion coefficient is zero.

problem has been treated by Schubert *et al.* (1970) who include the important effect of phase boundary distortion not accounted for in this divariant analysis.

Next, we consider the case where  $\alpha$  and  $\beta_a$  are non-zero in the two pure phase regions. We model the olivine-spinel transition by assuming  $d/D = 0.05$  and  $\bar{\alpha}/\alpha = 100$ . The results for  $R_{\beta_{crit}}$  as a function of  $R$ , the parameter which measures the stabilizing tendency of the increased adiabatic gradient in the two-phase region, are shown in Fig. 10. For  $R \lesssim 10^4$  the layer with this divariant phase transformation is more unstable to convection than is a single-phase fluid layer with the same width  $D$ . As  $R$  increases,  $R_{\beta_{crit}}$  also increases (the stabilizing effect of  $R$ ), rather slowly for  $R \lesssim 10^3$  and then more rapidly for  $R$  between  $\approx 10^3$  and  $\approx 10^5$ . For values of  $R$  above about  $10^6$ ,  $R_{\beta_{crit}}$  levels off at a value of about 1900; the dashed portion of the stability curve represents values of  $R_{\beta_{crit}}$  computed only approximately.

The large increase in  $R_{\beta_{crit}}$  at  $R$  of around  $10^4$  can be understood as follows. The corresponding critical Rayleigh number in the two-phase region  $\bar{R}_{\beta_{crit}}$  is  $(\bar{\alpha}/\alpha)R_{\beta_{crit}} - R$ . For  $R \lesssim 10^4$ ,  $\bar{R}_{\beta_{crit}}$  is positive, which means that  $\bar{\beta}_a < \beta_{crit}$ . Thus the undisturbed critical temperature gradient exceeds the adiabatic temperature gradient even in the

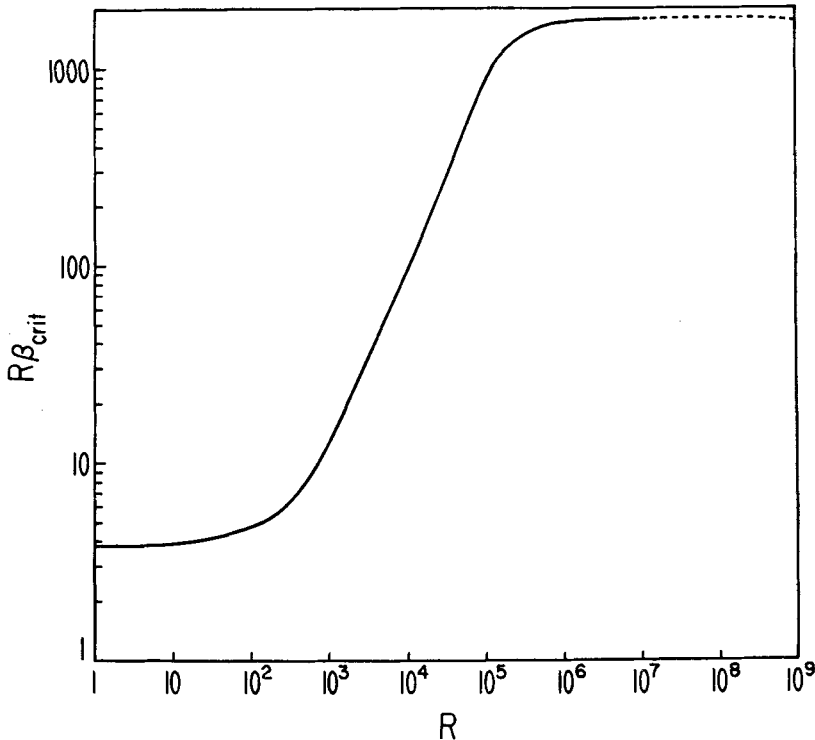


FIG. 10. The critical Rayleigh number  $R_{\beta_{crit}}$  for onset of convection in a fluid layer with a divariant phase transition zone.  $d/D = 0.05$  and  $\bar{\alpha}/\alpha = 100$ .  $R$ , the parameter relating the magnitudes of the adiabatic temperature gradients in the two-phase and single-phase regions is proportional to  $(\beta_a - \beta_a)$ .

two-phase divariant region and with the increased buoyancy of this region the entire layer is more unstable than a layer without the phase change. For  $R \gtrsim 10^4$ ,  $\bar{R}_{\beta_{crit}}$  is negative and  $\bar{\beta}_a > \beta_{crit}$ . The undisturbed critical temperature gradient is smaller than the adiabatic gradient in the two-phase region and this stabilizing effect manifests itself by increased values of  $R_{\beta_{crit}}$ . The stabilizing effect 'saturates', however, since  $R_{\beta_{crit}}$  is insensitive to further increases in  $R$ , for  $R$  sufficiently large.

As in the univariant stability analysis, the quantitative divariant stability results from Fig. 10 can be recast into a plot of  $(\beta - \beta_a)_{crit}$  vs  $\nu$ , shown in Fig. 5 (we assumed  $\bar{\beta}_a - \beta_a = 1.5^\circ\text{K km}^{-1}$  in this computation). Qualitatively, there is little difference between the univariant and divariant stability curves of Fig. 5. The same conclusions which were drawn about convection through the olivine-spinel phase change based upon a univariant stability analysis apply to the phase transformation when analysed from the divariant approach. Convection is possible through a divariant phase transition zone, and may even be enhanced by the phase change, for reasonable values of the thermal and rheological properties of the Earth's mantle.

#### Application to the descending slab

The phase changes in the descending lithosphere at oceanic trenches provide a striking finite-amplitude example of the interaction of phase transformations and mantle convection. In this section, we discuss both the olivine-spinel and spinel-oxide

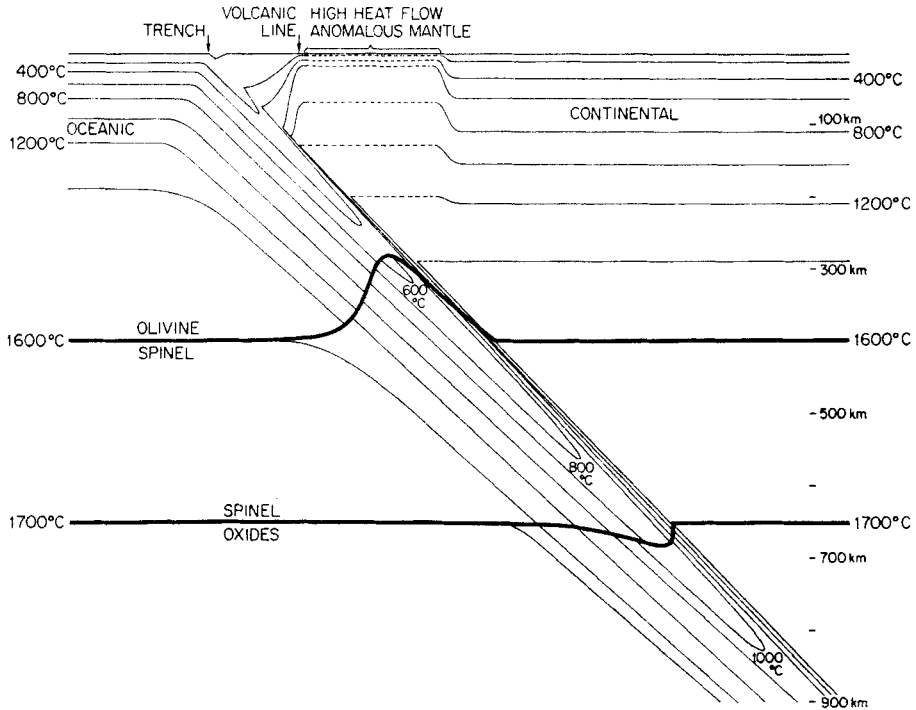


FIG. 11. Thermal structure of the descending lithosphere including the effects of frictional heating on the slip zone and the olivine-spinel and spinel-oxide transitions. The thin lines denote the isotherms and the heavy lines represent the positions of the phase changes. The velocity of the plate approaching the trench is  $8 \text{ cm yr}^{-1}$ . Other parameter values are given in the text. Note the relatively large elevation of the olivine-spinel phase change and the relatively small depression of the spinel-oxide transition in the slab.

transitions in the descending slab based on the assumptions that the slab penetrates the lower phase change and that this transition is indeed endothermic.

Many authors have considered the temperature distribution in the descending slab (McKenzie 1969, 1970; Hasebe *et al.* 1970; Oxburgh & Turcotte 1970; Minear & Toksöz 1970a, b; Toksöz *et al.* 1971; Griggs 1972). Following the first studies of the elevation of the olivine-spinel phase boundary in the descending slab (Schubert *et al.* 1970; Schubert & Turcotte 1971), subsequent calculations (Turcotte & Schubert 1971, 1973; Toksöz *et al.* 1971) included this effect. In Fig. 11 we show the thermal structure of a typical descending slab including the olivine-spinel and spinel-oxide phase changes.

Determination of the thermal structure of a descending slab requires many assumptions. Temperatures within the rigid slab are subject to the least error since the rheological properties of the material are known. The temperature distribution given in Fig. 11 is based on the calculations of Turcotte & Schubert (1973). The angle of dip is  $45^\circ$  and the velocity of the plate approaching the trench is  $8 \text{ cm/yr}$ . Within the slab we assume the thermal conductivity  $k$  is  $10^{-2} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$  and the thermal diffusivity  $\kappa$  is  $1.15 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ . On the upper boundary of the descending slab frictional heating occurs until the melt temperature is reached along the slip zone. The frictional heating is produced by a constant coefficient of friction  $f = 0.054$ . It is assumed that the melt temperature  $T_m = 1000^\circ \text{C}$ . This value may be several hundred degrees too high or too low depending on the water content of the descending crust,



as discussed by Wyllie (1973). The shear stress on the slip zone at the depth where  $T_m$  is attained is 2.04 kb. It is assumed that the volcanic line lies above the point on the descending slab where melting first occurs, in this case 125 km behind the trench. In fact, the observed location of the volcanic line was used to specify the frictional heating on the slip zone (Turcotte & Schubert 1973).

Behind the volcanic line a region of anomalously high heat flow and high seismic attenuation is often observed. The Sea of Japan is an example. We assume that this region extends 200 km beyond the volcanic line. We also assume that the temperature on the slip zone is buffered at the melt temperature beneath this region, i.e. to a depth of 325 km. The isotherms above the descending slab in this region can only be estimated; they are shown by dashed lines. Convective transport of heat by magmas may occur in this region, or a secondary flow process in the mantle may dominate. Behind the anomalous region the overlying mantle is assumed to have a typical continental geotherm (Froidevaux & Schubert 1975). Approaching the trench the oceanic plate is assumed to have a boundary layer geotherm (Turcotte & Oxburgh 1969) corresponding to a surface heat flow of  $0.8 \mu\text{cal cm}^{-2} \text{s}^{-1}$ . Beneath the boundary layer the oceanic geotherm is taken to be adiabatic. It is worth noting that at about 400 km depth, the calculated suboceanic and subcontinental temperatures are similar.

The changes in depth of the phase transitions in the descending slab are primarily determined by the magnitudes of the slopes of the Clapeyron curves. For the olivine-spinel phase change we take the value  $\gamma = 40 \text{ bar } ^\circ\text{K}^{-1}$  (Schubert & Turcotte 1971). Since the slope of the Clapeyron curve is positive for the olivine-spinel transition the boundary is elevated as shown in Fig. 11. The maximum elevation is 115 km. Also associated with the olivine-spinel phase change is a heat release  $Q = 40 \text{ cal/g}$  (at  $1600^\circ\text{C}$ ) which heats the descending slab. The result is the displacement of the isotherms across the phase boundary shown in Fig. 11.

For the spinel-oxide phase change, we take the slope of the Clapeyron curve to be  $\gamma = -13 \text{ bars } ^\circ\text{K}^{-1}$  (Ahrens & Syono 1967). Since the slope is negative the phase boundary is depressed in the descending slab (Fig. 11). The maximum depression is only 30 km. Also associated with this phase change is an absorption of heat  $Q = -18 \text{ cal g}^{-1}$ ; the temperature of the descending slab is decreased across the phase boundary resulting in the isotherm displacement shown in Fig. 11.

Clearly, the downward force on the descending slab is one of the important driving mechanisms for plate tectonics. Two contributions to this body force have been recognized (Schubert & Turcotte 1971), the negative buoyancy force associated with the thermal contraction of the slab and the elevation of the olivine-spinel phase boundary.

The body force per unit length parallel to the trench axis and per unit depth along the slab is given in Fig. 12. The coefficient of thermal expansion  $\alpha$  is taken to be  $3 \times 10^{-5} \text{ } ^\circ\text{K}^{-1}$  at the surface, decreasing to  $2 \times 10^{-5} \text{ } ^\circ\text{K}^{-1}$  at a depth of 900 km. The density increases associated with the olivine-spinel and spinel-oxide phase changes are taken to be  $0.24 \text{ g cm}^{-3}$  and  $0.4 \text{ g cm}^{-3}$ , respectively. Positive forces are down along the slab, negative forces up. The maximum downward force per unit depth and per unit length along the trench due to thermal contraction is 0.65 kb. The additional downward body force due to the olivine-spinel phase change is clearly shown between the depths of 285 km and 400 km. The maximum additional downward body force per unit depth and per unit length along the trench axis due to the olivine-spinel phase change is 2.6 kb. The upward body force due to the spinel-oxide phase change is shown between the depths 650 km and 680 km. The maximum upward body force per unit depth and per unit length of trench is 2.8 kb. The total gravitational body force on the descending slab to a given depth is the integral of the curve given in Fig. 2. The total downward body force due to the olivine-spinel phase change is considerably larger than the upward body force due to the spinel-oxide

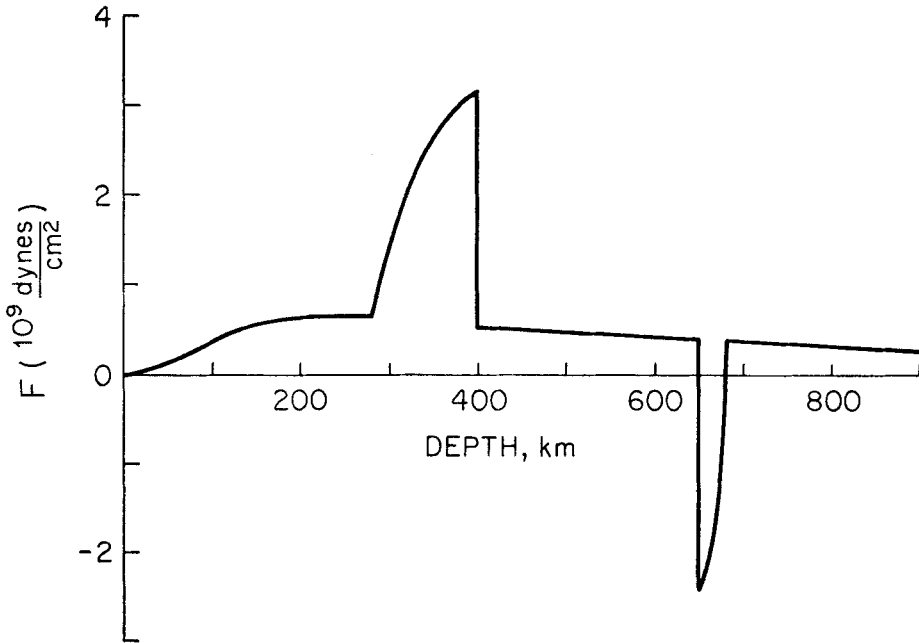


FIG. 12. The gravitational body force per unit distance parallel to the trench and per unit depth on the slab considered in Fig. 11. Thermal contrasts between the descending slab and the adjacent mantle and the vertical displacements of the two phase change boundaries relative to the surrounding mantle contribute to the body force.

phase change because of the larger displacement of the olivine–spinel phase change from its undisturbed equilibrium depth.

The upward body force due to the spinel–oxide phase change may be responsible for the predominance of compressional focal mechanisms in deep earthquakes between depths of 500 and 700 km (Isacks & Molnar 1971). Similarly, the downward body force due to the olivine–spinel phase change may be responsible for the tensional focal mechanisms associated with intermediate depth earthquakes between 100 and 300 km.

In the previous section on the effect of the spinel–oxide transition on the stability of a fluid layer, it was shown that for reasonable earth models the ‘mechanical brake effect’ due to this phase change is insufficient to prevent convection through this phase boundary. Our finite amplitude example of the descending lithosphere, wherein both major phase changes are incorporated, confirms that the net body force on the slab is downward, supporting the possibility that the downgoing slab indeed penetrates below the 650 km phase change. This is in contrast to the view that the lithosphere ceases to exist as a separate entity below 700 km due to the absence of earthquakes below this depth (Isacks & Molnar 1971; Mereu *et al.* 1974). From Fig. 11 we see that temperature contrasts of up to 700 °K between the slab and the adjacent mantle can exist down to depths of 800–900 km. Recent seismological evidence based on differential travel times (Jordan & Lynn 1974) imply strong lateral temperature contrasts of hundreds of degrees between 600 km and 1400 km beneath the Caribbean. This observation supports the above thermal calculations and provides evidence for the penetration of the descending slab to depths greater than that of the spinel–oxide transition.

Gilbert & Dziewonski (1975) from the temporal variation of the seismic moment tensor and the evidence of precursive compression for two deep earthquakes suggest that the compressive stress release may be due to a metastable phase transition (Dennis & Walker 1965). However, the reaction rate of the olivine–spinel phase change (Kasahara & Tsukahara 1971) is likely to be sufficiently rapid to suppress this non-equilibrium tendency (Ringwood 1972).

### Summary and conclusions

We have reviewed the physics of the stability of a fluid layer containing a univariant phase transition, identifying those effects which are stabilizing and destabilizing for both exothermic (olivine–spinel) and endothermic (spinel–oxide) reactions. Univariant phase change stability theory provides critical Rayleigh numbers  $R_{\beta_{\text{crit}}}$  for the onset of convection in a fluid layer which depend on  $R_Q$  a latent heat parameter and  $S$  a phase boundary distortion parameter. Values of  $R_{\beta_{\text{crit}}}$  have been given for the endothermic reaction for which  $R_Q$  and  $S$  are negative; earlier papers have presented the values of  $R_{\beta_{\text{crit}}}$  pertinent to the exothermic reaction where  $R_Q$  and  $S$  are positive. The critical Rayleigh numbers have been used to construct plots of  $(\beta - \beta_a)_{\text{crit}}$ , the minimum or critical superadiabatic temperature gradient required for the onset of convection, *vs*  $\nu$ , the kinematic viscosity of the fluid layer, for both the olivine–spinel and spinel–oxide transitions. A comparison of these critical Rayleigh numbers or temperature gradients with those for convection in a single phase layer or for separate convection above and below the phase change boundary delineate the range of parameters wherein the phase changes provide stabilizing or destabilizing influences on convection. Both the olivine–spinel and spinel–oxide transitions may promote instability in the Earth's mantle.

After deriving the correct form of the thermodynamic quantities required to describe a two-phase region in a divariant system, e.g. the effective coefficient of thermal expansion and the adiabatic temperature gradient, we presented the linearized stability theory for the onset of convection in a layer of fluid with a divariant phase transition. For the olivine–spinel phase change, an increased effective thermal expansivity in the two-phase region promotes instability, while an increased adiabatic temperature gradient in the transition zone provides a stabilizing effect. These effects are reversed in the spinel–oxide case where the effective two-phase thermal expansion coefficient is smaller than that of the pure phases and where the adiabatic temperature gradient in the transition zone  $\bar{\beta}_a$  is smaller than the adiabatic temperature gradient in the single phase regions  $\beta_a$ . Critical Rayleigh numbers are computed for the olivine–spinel phase change as a function of a dimensionless parameter proportional to  $(\bar{\beta}_a - \beta_a)$ . When the critical temperature gradient  $\beta_{\text{crit}}$  is larger than  $\beta_a$  and  $\bar{\beta}_a$ , the layer with the divariant phase change is more unstable than a single-phase fluid layer, whereas when  $\beta_{\text{crit}} > \beta_a$  but  $\beta_{\text{crit}} < \bar{\beta}_a$ , the phase change is stabilizing. One arrives at the same overall conclusions about the stabilizing or destabilizing nature of the mineralogical phase changes in the Earth's mantle independent of whether the transitions are viewed as univariant or divariant transformations.

We computed the thermal structure of the descending slab, including the effects of the olivine–spinel and spinel–oxide transitions. The olivine–spinel phase boundary is elevated 115 km and the spinel–oxide transition is lowered by 30 km in the slab. A net downward gravitational body force acts on the slab as a result of the two major phase transitions therein. The downward body force due to the olivine–spinel phase change may account for the tensional focal mechanisms associated with intermediate depth earthquakes while the upward body force of the spinel–oxide transition may be responsible for the predominance of compressional focal mechanisms in deep earthquakes.

We have demonstrated that mantle convection could penetrate the major mineralogical phase changes in the Earth's mantle; indeed, these phase changes may enhance the intensity of convection and play a major role as a driving force for plate tectonics.

### Acknowledgment

This work was supported by the National Science Foundation under grant GA-40749.

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