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A EUTECTIC IN CARBON-OXYGEN WHITE DWARFS ?

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Résumé.— Lorsque l'intérieur d'une naine blanche commencera à se geler, les phases coexistantes de solide et liquide auront les compositions divergentes. Deux modèles du diagramme de phases pour carbone-oxygène sont décrites. Pour le modèle plus réaliste, un eutectique marqué est prédit, et les phases coexistantes sont l'oxygène pur et le carbone pur. Le modèle prédit qu'une naine blanche commencera à se geler plus tard, et après elle se rafraîchira plus lentement.

Abstract.— When the interior of a white dwarf begins to freeze, the coexisting solid and liquid phases will have different compositions in general. Two models for the carbon-oxygen phase diagram are described. In the more realistic model, a pronounced eutectic is predicted and the solid phase is either pure carbon or pure oxygen. The model predicts that a white dwarf begins to freeze later in its evolution and then cools more slowly.

1. Introduction. — The possible importance to astrophysics of the alloying behaviour of dense Coulomb lattices was first considered in detail by Dyson (1971). His primary motivation was the physics of neutron star crusts, but essentially the same physics is relevant to white dwarf interiors. The question we pose is this: what happens when a white dwarf begins to freeze? Although the thermonuclear evolution prior to degenerate cooling is not yet fully understood, it is generally agreed that a white dwarf interior will consist of a mixture of elements in the mass range $4 \leq A \leq 56$ (atomic number range $2 \leq Z \leq 26$). The Gibbs phase rule demands that when this mixture begins to freeze, the coexisting solid and liquid will, in general, have different compositions. If, as seems likely, the miscibility properties of the solid and liquid phases are very different, then the coexisting phases may have very different compositions. This would have important implications for the evolution of very cold ($L \leq 10^{-4} L_{\odot}$) white dwarfs. Before proceeding with the question of solid-liquid equilibrium, a few words should be said about a liquid-liquid miscibility gap. This has been proposed for the hydrogen-helium mixture in the major planets (Stevenson, 1975) and it is now apparent that limited miscibility is a ubiquitous property of Coulomb mixtures (Stevenson, 1976; Bami et al., 1979). However, a liquid-liquid miscibility gap will only occur if the predicted critical temperature is greater than the freezing point of at least one of the end-members of the alloy. This may be marginally possible in white dwarfs in the case of iron dissolved in carbon (discussed by Stevenson, 1977) but is not likely for $Z \leq 26$. For example, the critical temperature in C-O

is only about 2×10^4 K (Stevenson, 1976) much less than the freezing point of either constituent at the pressures of interest. It is for this reason that attention is focussed here on the liquid-solid equilibrium. The discussion is further limited to the case of a carbon-oxygen white dwarf, since this is believed to be the most relevant situation (Shaviv and Kovetz, 1976).

By limiting ourselves to the carbon-oxygen case, we are greatly reducing the potential importance of gravitational differentiation as an energy source in cooling white dwarfs, since pure carbon and pure oxygen have almost the same mass density. (Remember that the density would be only a function of A/Z if the pressure were derived solely from the energy of the electron gas. Apart from isotope effects, $A/Z = 2$ in both carbon and oxygen). Nevertheless, even the small density difference (~ 1 part in 10^3) can have a significant effect. The presence of eutectic behaviour (i.e. greatly depressed freezing point) can change the cooling history, and the presence of differentiation can cause the atmosphere to evolve, even if the gravitational energy change is relatively small. We shall not attempt a detailed description of white dwarf evolution here (although some general comments are made in §4) but merely describe the likely phase diagram of C-O.

2. A simple model. — It has been shown previously (Stevenson, 1976) that simple modelling of Coulomb systems can reproduce or predict Monte Carlo calculations (Bami et al., 1979). The modelling described below should nevertheless be regarded only as provocation for a more detailed analysis. Atomic units are used throughout (i.e. $e = m = 1$).

It is first necessary to understand the pure elements.

The proposed model Helmholtz free energies per nucleus for the pure solid and pure liquid are

$$F_S = ZE_{eg}(r_s) - \frac{\alpha_s Z^{5/3}}{r_s} - k_B T S_s \quad (1)$$

$$F_L = ZE_{eg}(r_s) - \frac{\alpha_L Z^{5/3}}{r_s} - k_B T(S_s + \Delta S) \quad (2)$$

where Z is the nuclear charge, E_{eg} is the energy of the compensating electron gas, r_s is the usual electron spacing parameter, k_B is Boltzmann's constant, α_s and α_L are the Madelung constants for the solid and liquid phases respectively, S_s is the solid state entropy at the melting point (assumed constant, in the spirit of Lindemann's "Law") and S is the entropy difference between the phases. We expect $\Delta S \approx \ln 2$ (Stishov, 1975). At a given pressure, the value of r_s will differ slightly between the phases because $\alpha_s \neq \alpha_L$. Equating Gibbs energies, the melting point T_M for this model is given by

$$T_M = \frac{(\alpha_s - \alpha_L) Z^{5/3}}{k_B \Delta S r_o} \quad (3)$$

where r_o is the value of r_s that would be obtained if all the pressure P were due to the electron gas:

$$P = - \frac{1}{4\pi r_o^2} \left. \frac{dE_{eg}(r_s)}{dr_s} \right|_{r_o} \quad (4)$$

Equation (3) is consistent with the Monte Carlo results, provided one chooses $\alpha_s - \alpha_L \approx \Delta S/155$ (Pollock and Hansen, 1973).

The free energies of the solid and liquid alloys are obtained by adding the ideal entropy of mixing and by assuming ion-sphere charge averaging (Salpeter, 1954; DeWitt, 1978) which states that the electrostatic energy per nucleus is $-\alpha Z^{5/3}/r_s$, where $\alpha = \alpha_L$ or α_s depending on the phase, and $Z^{5/3} = x Z_1^{5/3} + (1-x) Z_2^{5/3}$, where Z_1, Z_2 are the two nuclear charges present and x is the number fraction of species 1. As we discuss in the next section, this may be a poor approximation for the solid alloy, but it appears to work well for the fluid mixture, based on Monte Carlo results (DeWitt, 1978; Brami et al., 1979).

Neglecting the unimportant S_s , the resulting chemical potentials are then

$$\mu_{s,1} \approx \mu_1^o - \frac{\alpha_s Z_1^{5/3}}{r_o} + k_B T \ln x_s \quad (5)$$

$$\mu_{L,1} = \mu_1^o - \frac{\alpha_L Z_1^{5/3}}{r_o} + k_B T \ln x_L - k_B T \Delta S \quad (6)$$

$$\mu_{s,2} = \mu_2^o - \frac{\alpha_s Z_2^{5/3}}{r_o} + k_B T \ln(1-x_s) \quad (7)$$

$$\mu_{L,2} = \mu_2^o - \frac{\alpha_L Z_2^{5/3}}{r_o} + k_B T \ln(1-x_L) - k_B T \Delta S \quad (8)$$

$$\mu_i^o = Z_i E_{eg}(r_o) + \frac{4}{3} \pi r_o^3 Z_i P \quad (9)$$

where subscript 1 or 2 refers to the nuclear species of charge Z_1 or Z_2 respectively, and the subscripts s and L refer to solid and liquid alloys.

Equating $\mu_{s,1} = \mu_{L,1}$ and $\mu_{s,2} = \mu_{L,2}$, and using equation (3) we find that the equilibrium carbon number fractions for liquid and solid

$$x_L = \frac{1 - \exp\left[-\Delta S \left(\frac{T}{T_o} - 1\right)\right]}{1 - \exp\left[-\Delta S \left(\frac{T}{T_o} - \frac{T}{T_c}\right)\right]} \quad (10)$$

$$x_s = x_L \exp\left[\Delta S \left(\frac{T_c}{T} - 1\right)\right] \quad (11)$$

where T_c and $T_o \approx 1.615 T_c$ are the freezing points of pure carbon and pure oxygen, respectively.

In figure 1, the resulting phase diagram is shown, assuming $\Delta S = \ln 2$. Even this model, which effectively minimizes the difference between solid and liquid phases, predicts a significant difference between the compositions of coexisting phases. For example, a 50-50 fluid mixture is in equilibrium with a solid of 58 % oxygen, 42 % carbon by number. This phase diagram is compatible with the Monte Carlo calculations of Loumos and Hubbard (1973).

Fig. 1 : C-O phase diagram. Shading is the phase-excluded region. Error bar denotes Monte Carlo simulation (Loumos and Hubbard, 1973).

3. An improved model. - The above model may be incorrect because it assumes the existence of a solid alloy in which both the electrostatic energy is favorable (i.e. close to ion-sphere charge averaging) and the entropy is favorable (i.e. close to the ideal entropy of mixing). In fact, it is not possible to achieve this. Dyson (1971) found that ordered alloys (for example, the CsCl structure) were close to ion-sphere charge averaging but these alloys have no entropy of mixing. Straus et al. (1977) found that the solid H-He alloy prefers disorder since this raises the entropy (lowers the free energy) even though the electrostatic energy is unfavorable. The physical consequence of this is that a liquid alloy is much more readily formed than a solid alloy. This leads to a pronounced eutectic and almost pure coexisting solid phases, a common situation in metallurgy.

Here, we consider a model in which the solid alloy has an ideal entropy of mixing and the electrostatic energy of a random alloy (i.e. no compositional order, even at short range). This is admittedly an extreme assumption, but it is likely to be closer to reality than the situation illustrated in Figure 1. The electrostatic energy of the solid is now $-\alpha_s \bar{Z}^{5/3}/r_s$ where $\bar{Z} = xZ_1 + (1-x)Z_2$. The following chemical potentials are obtained

$$\mu_{s,1} = \mu_1^0 - \frac{\alpha_s f}{r_o} + k_B T \ln X_s \quad (12)$$

$$\mu_{L,1} = \mu_1^0 - \frac{\alpha_L Z_1^{5/3}}{r_o} + k_B T \ln X_L - k_B \Delta S \quad (13)$$

$$\mu_{s,2} = \mu_2^0 - \frac{\alpha_s f}{r_o} + k_B T \ln (1-X_s) \quad (14)$$

$$\mu_{L,2} = \mu_2^0 - \frac{\alpha_L Z_2^{5/3}}{r_o} + k_B T \ln (1-X_L) - k_B \Delta S \quad (15)$$

$$f_i = \frac{5}{3} Z_i \bar{Z}^{2/3} - \frac{2}{3} \bar{Z}^{5/3} \quad (16)$$

In this case, we must separately consider the carbon rich and oxygen-rich sides of the phase diagram. On the carbon-rich side, we find

$$k_B (T-T_C) \Delta S + k_B T \ln \left(\frac{X_s}{X_L} \right) \approx - \frac{2.94 (1-X_s)^2 \alpha_s}{r_o} \quad (17)$$

Since $2.94 \alpha_s / r_o > k_B T_C$, it follows that the solution to this is

$$X_s \approx 1$$

$$X_L \approx \exp \left[\Delta S \left(1 - \frac{T}{T_C} \right) \right] \quad (18)$$

Phase equilibrium is therefore between a pure carbon solid and a fluid mixture at a temperature less than the melting point of pure carbon.

Similary, equilibrium on the oxygen-rich side of the phase diagram is given by

$$k_B (T-T_O) \Delta S + k_B T \ln \left(\frac{1-X_s}{1-X_L} \right) \approx - \frac{1.18 \alpha_s X_s^2}{r_o} \quad (19)$$

which has the solution

$$X_s \approx 0$$

$$X_L \approx 1 - \exp \left[\Delta S \left(1 - \frac{T}{T_O} \right) \right] \quad (20)$$

The eutectic is the solution of

$$\exp \left[\Delta S \left(1 - \frac{T}{T_O} \right) \right] + \exp \left[\Delta S \left(1 - \frac{T}{T_C} \right) \right] = 1 \quad (21)$$

and is given by $T = 0.628 T_C (=0.389 T_O)$ and $X_L = 0.668$ (assuming $\Delta S = \ln 2$). The phase diagram is shown in Figure 2. It is only marginally consistent with the Monte Carlo calculations of Loumos and Hubbard (1973). However, Monte Carlo simulations are not likely to simulate eutectic behaviour directly, because of relaxation problems, the identification of a eutectic may require the type of approach used by Hansen and coworkers, in which analytic approximations to the free energies are derived and the phase boundaries calculated (e. g. Pollock and Hansen, 1973).

Fig. 2 : An improved model for the C-O phase diagram. Shading represents phase-excluded region. Error bar denotes Monte Carlo simulation (Loumos and Hubbard, 1973).

4. Implications. - Consider a white dwarf whose interior consists of a 50-50 mixture of carbon and oxygen. What happens as this star freezes?

In the case of the phase diagram of Figure 1, the solid which initially freezes is about 58 % oxygen, and the freezing begins at a temperature about halfway between the two pure freezing points T_C and T_O . The solid is slightly heavier and settles to the bottom, leaving behind a fluid that is slightly depleted in oxygen. Despite the subadiabatic temperature gradient, convection is now possible in the form of "salt fingers" (Spiegel, 1972) because thermal diffusion is much more rapid than solute diffusion. The result is likely to be a uniformly mixed fluid region (up to the atmosphere), slightly depleted in oxygen, and a coexisting oxygen-rich core. However, the modest difference in composition between coexisting phases would mean that the gravitational energy release is very small and the redistribution of elements is slight. In the case of the phase diagram of Figure 2, the effect is far more striking. First, we see that the onset of freezing is delayed because of the pronounced eutectic behaviour. Once freezing begins, almost pure solid oxygen settles from the mixture leaving behind a slightly oxygen-depleted fluid which rehomogenizes because of the "salt finger" instability. This fluid will evolve along the phase boundary towards the eutectic composition. At the same time, a significant amount of energy is released gravitationally. By the virial theorem, most of this energy is radiated away. Phase separation is thus a negative feedback mechanism: it slows the rate at which the star cools. The atmosphere composition might also change as the fluid below becomes progressively carbon-rich. When the eutectic is reached, pure solid carbon can also form: this will rise and re-dissolve higher up, aiding the differentiation. (Metallurgists talk of the eutectic as a point at which the fluid can freeze directly without compositional change. In a very slowly cooling system, however, gravity will ensure the physical separation of carbon and oxygen snowflakes). The final state will be an almost completely differentiated body: a solid oxygen core and an overlying solid carbon mantle.

It must be stressed that the primary purpose of this paper is to provoke further study, both of the phase diagram (by Monte Carlo techniques) and of the stellar evolution. The present observational situation is unclear (Liebert et al., 1979) but there is a suggestion that the white dwarf population is incompatible with simple cooling curves.

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