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Low-temperature instability of intermetallic phases.

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The thermodynamic criterion for the stability of an intermetallic phase or compound A_mB_n with respect to the components A and B at a given temperature and pressure is well known to be

$$A_mB_n \rightleftharpoons mA+nB \qquad \Delta F>0,$$
$$\Delta F=\Delta H-T\Delta S.$$

The possibility thus exists that some intermetallic phases may be formed from the elements with the absorption of heat ($\Delta H>0$), and still be stable at elevated temperatures because of the term $-T\Delta S$. Assuming no change with temperature of ΔH and ΔS, we should expect that such compounds become unstable with respect to the free elements at lower temperatures.

A survey of the literature shows that endothermic intermetallic 'compounds', resulting from combinations among the elements gold, mercury, thallium and lead, are sometimes found (Weibke & Kubaschewski, 1943).

Recent thermodynamic investigations by one of the authors (Kleppa, 1949) indicate an endothermic process for the phase Au_2Pb which is formed peritectically from practically pure gold and the liquid solution at 418° C. (Hansen, 1936). For the formation of one gram molecule of this phase from the pure liquid elements at 400° C. calculation gave $\Delta H=-2\cdot0\pm0\cdot1$ kcal. By combination with the accepted values for the heats of fusion for gold and lead, and making the additional assumption that there is no change in specific heat on fusion for these two elements, we find that the ΔH of formation for Au_2Pb is $\sim+0\cdot5$ kcal./g. molecule at 400° C.

One would expect that at lower temperatures this compound would break down to give free gold and free lead, or some other intermetallic phase, by a diffusion transformation which would be very slow. It was hoped, however, that a suitable combination of cold work and correct temperature would speed the decomposition.

The compound Au_2Pb was prepared by melting 99·9% pure gold with 99·98% pure lead 0·1% in excess of the stoichiometric proportion, and annealing the ingot in vacuum 100 hr. at 400° C. to eliminate segregation. The diffraction pattern of the annealed material showed only the lines of Au_2Pb (Perlitz, 1934).

All analysis for phases present was done by X-ray diffraction, using the General Electric XRD-3 X-ray spectrometer.

The Au_2Pb phase is very brittle, so cold working was done by crushing in a 'diamond' mortar. It was found that as the material was reduced to a powder small plates formed indicative of some ductile material present as a binder. These plates were brittle and readily reduced to a powder in an agate mortar. Both the plates and the powder gave diffraction patterns of Au_2Pb plus gold. An estimated maximum of 30–50% transformation was obtained.

In the as-worked condition the lines are quite broad, owing to strain and probably to small particle size, but annealing in vacuum for 1–2 hr. at 300° C. sharpens the lines with no detectable change in the amounts of the two phases present.

The other decomposition product almost certainly is $AuPb_2$, though it was found only in two specimens that had been crushed in oil and annealed in vacuum at 200° C. The strongest $AuPb_2$ lines lie close to strong Au_2Pb lines and may be present but unresolved in other specimens.

Lattice-parameter determinations gave for the Au_2Pb both in the pure and partially transformed material $7\cdot93\pm0\cdot01$ A. and for the gold in the transformed material $4\cdot078\pm0\cdot003$ A., the same as pure gold within the limits of error.

Annealing the transformed material 48 hr. at 400° C. returned it to the single phase, Au_2Pb.

Work is being continued to determine the decomposition products and the equilibrium temperatures.

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The one-dimensional crystal. III. A punched-card method for computing structure factors.

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Two methods for calculating structure factors on International Business Machines have already appeared in this *Journal* (Donohue & Schomaker, 1949; Grems & Kasper, 1949). The present method, however, may still be of interest because it is straightforward and particularly rapid for crystals of low symmetry.

The position of each atom is determined by only one co-ordinate, X; the reflection hkl is designated by only one index, H; the angle HX is expressed in cycles:

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$1^{c} = 2\pi$ radians (Donnay & Donnay, 1949). We want to calculate

$$A_H = \sum_{n=1}^{N} f_n \cos HX_n \quad \text{and} \quad B_H = \sum_{n=1}^{N} f_n \sin HX_n.$$

For each of the N atoms in the cell, one card is prepared in which are hand-punched: a number j identifying the kind of atom, the running index n, and the co-ordinate X_n of the atom. This master set of N cards is reproduced as many times as there are reflections and, simultaneously, each set has its H value with corresponding $(\sin\theta)/\lambda$ (rounded off to 0·005) gang-punched into it. Then H is multiplied by X_n on the calculating punch (type 602) and the decimal part of the product, rounded off to three places, is punched into the data cards. Sort the cards on HX_n and merge with a set of one thousand 'function cards' that carry the values of α, $\sin\alpha$ and $\cos\alpha$, from $\alpha = 0{\cdot}000$ to $\alpha = 0{\cdot}999$ at intervals of 0·001 cycle. HX_n and α are used as control fields. By intersperse gang-punching the $\cos HX_n$ and $\sin HX_n$ values are transferred from the function cards on to the data cards. Sort on $(\sin\theta)/\lambda$ and on j, an operation which removes the function cards. Merge each of the j groups of data cards, on $(\sin\theta)/\lambda$ as control field, with the corresponding set of 'f_j cards'. These f_j cards are prepared once and for all; they carry $(\sin\theta)/\lambda$, j, and f_j for $(\sin\theta)/\lambda$ going from 0·000 to 1·500 at intervals of 0·005. The 602 punch is wired to multiply $\cos HX_n$ and $\sin HX_n$ by f_j and to punch the products into the data cards. Finally, sort on H or $(\sin\theta)/\lambda$, depending on the order in which the reflections are to be listed. The tabulator will print for each reflection: H, $(\sin\theta)/\lambda$, j, n, f_j, the contributions of each atom to A_H and B_H, as well as the sums A_H and B_H.

We wish to thank the Watson Scientific Computing Laboratory for the permission to use their machines and Mr Eric Hankam for his kind assistance in preparing the control panels.

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Three new polymorphs of silicon carbide, 8*H*, 75*R*, and 84*R*.

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Three new polymorphs of silicon carbide have recently been discovered at the Mineralogical Laboratory, University of Michigan. The first of these has an eight-layered hexagonal unit cell, and is designated as type 8*H*. The crystal is an intergrowth of the new type with the more common 6*H*. Its structure has been established as having the zig-zag sequence 44 (Ramsdell, 1947). The second polymorph is rhombohedral and has a unit cell of 75 layers. The zig-zag sequence of type 75*R* is found to be 3232322323 (repeated three times). This structure was deduced by considering sequences involving only the numbers 2, 3 and 4, since no others have been observed in any of the known hexagonal or rhombohedral forms of silicon carbide.

The third polymorph is also rhombohedral and is an intergrowth with type 6*H*. On the basis of direct measurements on the Weissenberg photographs, it was not absolutely certain whether this new type is 81*R* or 84*R*. Using the same empirical limitation mentioned above, the only plausible solution seemed to be an 84-layered unit cell, with a zig-zag sequence of either 3333333232 or 3333323332 (each repeated three times). Intensity calculations have proved the first of these arrangements to be the correct one. The fact that the unit cell has 84 layers, rather than 81, was subsequently verified by the use of a Laue photograph, as suggested by Honjo, Miyake & Tomita (1950). In the Laue photograph, taken with a crystal-to-film distance of 6·5 cm., the resolution of the individual reflections is so much greater than on the Weissenberg films that there is no uncertainty in establishing the 84-layer character of this polymorph.

It will be noticed that neither of these two new rhombohedral types fits into the series proposed by Ramsdell (1947). This suggests the existence of a large number of additional polymorphs, the discovery of which may be effected by continued research. Several Weissenberg photographs obtained recently in our laboratory already indicate some new modifications.

In the near future the authors intend to describe, in a more detailed manner, these three new types of silicon carbide, and to discuss some structural implications of the ever-increasing number of polymorphs of this most unusual compound.

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Concerning reported discrepancies between X-ray and macroscopic measurements of thermal expansion of some alkali halides.

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A question of fundamental importance in the study of real crystals is the possibility of serious discrepancies in the values of those physical properties, such as thermal expansion, which may be studied by both X-ray and