Phase Transformations in Uranium at High Pressures*

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The α–β, β–γ and the direct α–γ phase transformations in uranium have been studied up to 45 kbar at cooling and heating rates of 3–5°C/sec. The overheating and undercooling intervals for the α–β and β–γ transformations at high pressures are about the same as the hystereses expected at zero pressure and do not vary appreciably with increasing contamination. Progressive contamination and resultant lowering of the transformation temperatures of the uranium samples was evident for all containers used, but was least for tantalum containers. The equilibrium α–β–γ triple point occurs at less than 31.5 kbar and greater than 803°C. The γ phase is definitely more compressible than the β phase and the β phase is probably more compressible than α. There is only a small hysteresis in the α–γ transformation.

URANIUM exhibits three well-recognized polymorphs—the so-called α, β and γ forms. The structures[1] are, respectively, orthorhombic (4 atoms/unit cell), tetragonal (30 atoms/unit cell) and body-centered cubic. There are distinct hystereses between transitions upon heating and cooling but careful work[2] has suggested that the equilibrium transformation temperatures are; α–β, 667.7°±1.3°C and β–γ, 774.8°±1.6°C.

The present experiments were undertaken in order to determine the courses of the α–β and β–γ transformations in uranium under pressure, to determine the coordinates of the α–β–γ triple point (which is readily predicted from zero-pressure data) and to investigate the direct α–γ transition. The only previous investigations of uranium at high pressure appear to be those of Bridgman,[3,4] in which no discontinuities in volume to 100 kbar or resistance to[5] 75 kbar were detected at room temperature.

It was anticipated that some problems with the contamination of uranium by the encapsulating material might arise during the prolonged high temperature work. This expectation was, unfortunately, borne out by the experiments. An attempt is made to delineate the effects of the alloying on the phase transformations.

I. EXPERIMENTAL PROCEDURES

Pressures up to 45 kbar were generated by a carboloy piston moving into a supported carboloy pressure vessel, $\frac{1}{2}$ in. in diameter by 2 in. long. Talc was used as the pressure-transmitting medium. The apparatus has been described *in extenso* previously.[6] Corrections for friction were made by comparing points on the investigated phase boundary, obtained on the increasing and decreasing pressure cycle. Corrections made in this way were not entirely consistent because of the progressive contamination of the uranium, which resulted in a lowering of the transformation temperatures. These estimates of friction were then augmented with estimates based on previous experience with the present geometry. Typical double-value friction corrections were 5.6 kbar at 40 kbar, 5.0 kbar at 30 kbar, 4.0 kbar at 15 kbar, etc. Pressures are believed accurate to ±0.5 kbar.

Phase transformations were detected by means of differential thermal analysis. The technique has been previously described.[6,7] Since reliable pressure corrections for Chromel-Alumel thermocouples are not yet available, values from the standard tables were used. Transformation temperatures were obtained both on heating and cooling, at typical rates of 3–5°C/sec, and were determinable to ±3°C.

The problem of finding a suitable, nonreactive encapsulating material proved to be severe and is discussed in detail with the presentation of the experimental results. Uranium was provided by the Lawrence Radiation Laboratory in the form of machined cylinders, of 0.142-in. diam by 0.175-in. length, with the primary impurity about 0.02 at.% oxygen.

The chronology of a given run was typically as follows: The uranium sample was cleaned with emery paper to expose the bright metallic surface and then both sample and container were washed with acetone. The sample was pushed into the container and covered with a tightly fitting lid. No lid was provided for the boron nitride containers; however, direct contact of the chromel-alumel thermocouple with the sample was avoided by means of a thin wafer of a good thermal conductor. To this end, a 10-mil wolfram sheet and a 20-mil piece of diamond cleavage plate were used in separate runs. After assembly in the press and applica-

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[1] A. N. Holden, *Physical Metallurgy of Uranium* (Addison-Wesley Publishing Company, Inc., Cambridge, 1958).

[2] B. Blumenthal, J. Nucl. Mater. 2, 23 (1960).

[3] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 76, 55 (1948).

[4] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 81, 169 (1952).

[5] All pressures revised, as appropriate, in accord with the scale based on the fixed points determined by G. C. Kennedy and P. N. LaMori, in *Progress in Very High Pressure Research*, edited by F. Bundy, W. R. Hibbard, and H. M. Strong (John Wiley & Sons, Inc., New York, 1961).

[6] G. C. Kennedy and R. C. Newton, *Solids Under Pressure* (McGraw-Hill Book Company, Inc., New York, 1962).

[7] A. Jayaraman, W. Klement, R. C. Newton, and G. C. Kennedy, J. Phys. Chem. Solids (to be published).

tion of some initial pressure, the sample was heated to about 600°C. The desired pressure was then applied and the sample carried through the transformations while the thermal arrest was recorded. The thermal arrests were usually pronounced and easily identified.

The transformation temperatures, both on heating and cooling, were recorded upon increasing compression, and upon the decrease of pressure. After releasing the pressure to very low values, a second compression cycle was run. The maximum temperature for any run was 850°C and the entire run was typically completed in less than an hour.

II. EXPERIMENTAL RESULTS

Blumenthal[2] has demonstrated the effects of cooling and heating rate on the α–β and β–γ transformations in high-purity uranium. The equilibrium transformation temperatures[2] of 667.7 ± 1.3°C (α–β) and 774.8 ± 1.6°C (β–γ) were obtained only by logarithmic extrapolations to a very low heating and cooling rates. For the heating and cooling rates used in the present experiments, the same extrapolations would place the transformations in high-purity uranium at zero pressure at the following temperatures; $\alpha \rightarrow \beta$, about 680°C; $\beta \rightarrow \gamma$, about 783°C; $\gamma \rightarrow \beta$, about 774°C, $\beta \rightarrow \alpha$, about 650°C.

Runs in Tantalum, Molybdenum, and Wolfram Containers

Results for the runs in tantalum, upon heating, are shown in Fig. 1. The data obtained on increasing pressure only are plotted since the temperatures for the decreasing pressure cycle were a few degrees lower due to increasing contamination. Transformation temperatures were found to be $\sim$10°C lower on the second compression, and this was taken as evidence for progressive contamination of the uranium. In the Ta II run, after one determination of the transformation temperatures in the lower pressure range, the pressure was increased directly to the vicinity of the triple point so as to determine accurately its coordinates with minimal contamination and to verify the pronounced
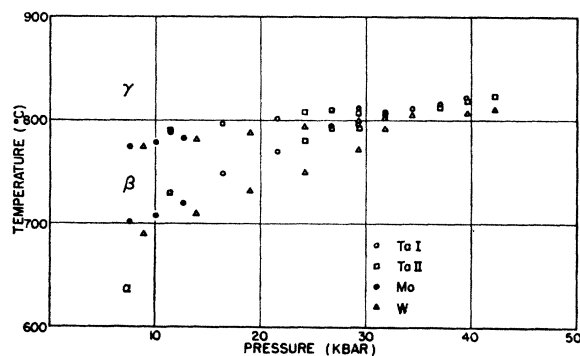

FIG. 1. Transition temperatures obtained for uranium encapsulated in tantalum, molybdenum, and wolfram.

curvature of the β–γ boundary. As seen in Fig. 1, this curvature is reproducible. The coordinates of the triple point are given in Table I, with due correction for the hysteresis. Also given in Table I are the hysteresis intervals, which are about the same as suggested by Blumenthal's[2] zero-pressure data and extrapolations; there does not appear to be any appreciable variation of these hystereses with pressure or with increasing contamination, as verified from measurements during the second and/or third cycles.

A few low-pressure points were obtained for uranium encapsulated in molybdenum before a thermocouple failure terminated the run. These temperatures fell significantly lower than those for the tantalum runs at the same pressures (Fig. 1). The single run in wolfram also yielded temperatures much lower than those for tantalum at the same pressures, the α–β transformation temperature being lowered proportionately more (Fig. 1). Other data for the molybdenum and wolfram runs are given in Table I.

TABLE I. Data for the uranium transformations in the various containers.

Container	Temperature interval between heating and cooling (°C)			Coordinates of triple point (on heating)	
	α–β	β–γ	α–γ	α–β–γ	
Tantalum	23–27	6–8	$\sim$5	30.5 ±0.5 kbar,	807 ±3°C
Wolfram	$\sim$22	$\sim$8	arrest too faint	33 ±1 kbar,	800 ±4°C
Molybdenum	$\sim$23	$\sim$5	not attained		
Copper	$\sim$22	$\sim$7	arrest too faint	35.8 ±1.0 kbar,	794 ±5°C
Silver	$\sim$25	$\sim$8	$\sim$2	33.8 ±0.6 kbar,	799 ±3°C
Boron nitride (W)	16–20	$\sim$5	not attained		
Boron nitride (diamond)	$\sim$18	$\sim$7		not attained	

Runs in Copper, Silver, and Boron Nitride Containers

Results for the runs in copper and silver, upon heating, are presented in Fig. 2. The coordinates of the triple points and the hysteresis intervals are given in Table I. The triple points are shifted to higher pressures relative to tantalum, mainly due to the greater lowering of the α–β transition temperatures. The maximum in the β–γ transition temperatures is also apparent for the uranium encapsulated in copper and silver.

No triple points were encountered for the uranium samples run in BN (Fig. 2). This was due mainly to the disproportionate lowering of the transition temperatures. The hystereses (Table I) were similar to those found in the other runs.

III. DISCUSSION OF RESULTS

From zero-pressure values of the entropy[8] and volume[1] changes of the α–β and β–γ transitions and assuming equal compressibilities and no change in the entropies with pressure and temperature, the α–β–γ triple point is calculated to be near 40 kbar and 855°C

[8] R. Hultgren et al. "Thermodynamics of Metals and Alloys," University of California, Berkeley (unpublished).

(slopes of 4.8^+ and 2.1^+ °C/kbar for the α–β and β–γ transitions, respectively). This naïve prediction was not realized for several reasons.

First, the assumption of equal compressibilities among the polymorphs is not satisfied. It might be very strongly expected that the softer[3] γ-uranium phase is considerably more compressible than the β phase. The maximum in the β–γ transformation temperatures just below the triple point for the Ta I and Ta II runs provides striking support for this contention. The possibility that another phase boundary with γ might originate at this "hump" was considered but a careful search for additional thermal arrests at higher temperatures was fruitless. The large hysteresis in the α–β transition precludes any definite conclusions, but it seems that there is some curvature to the α–β phase boundary, i.e., β uranium is somewhat more compressible than the α form.

Second, there was the general lowering of the transformation temperatures by progressive contamination.
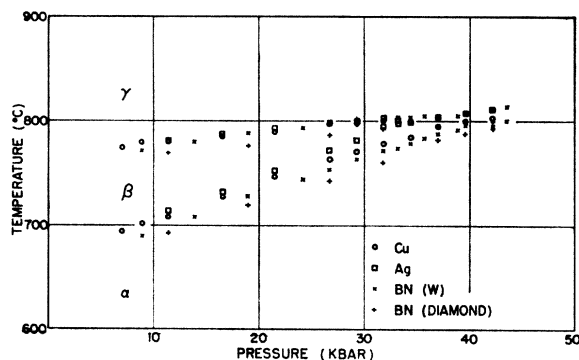

FIG. 2. Transition temperatures obtained for uranium encapsulated in copper, silver, and boron nitride.

The extent of this alloying cannot be effectively estimated. In Fig. 3 are given the temperatures recorded on heating and cooling for Ta I (and essentially substantiated in the Ta II run). Using these temperatures as lower bounds, the transformation ranges for uncontaminated uranium are proposed; by scaling the equilibrium temperatures relative to the hysteresis interval after Blumenthal,[2] the equilibrium phase boundaries are then suggested (Fig. 3). There is good agreement between the values obtained from Blumenthal's work[2] and the extrapolations to zero pressure of the hysteresis intervals proposed here for a 3–5°C/sec rate.

Third, in the absence of reliable thermocouple calibrations at higher pressures, there is little assurance that the temperatures herein published are not lower than the true values. Some preliminary work[9] indicates, however, that the corrections for Chromel-Alumel thermocouples should be less than 1% at 50 kbar.

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[9] *Progress in Very High Pressure Research*, edited by F. P. Bundy, W. R. Hibbard, and H. M. Strong (John Wiley & Sons, Inc., New York, 1961).
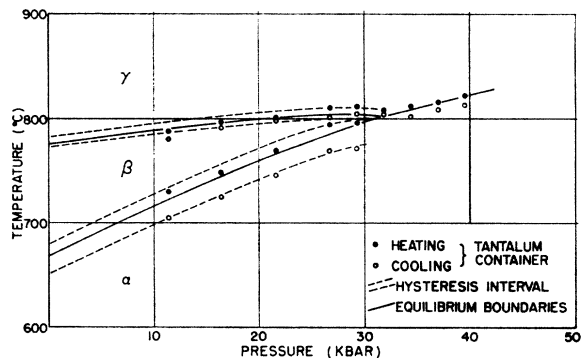

FIG. 3. Phase diagram for uranium obtained by heating and cooling at 3°–5°C/sec, sample encapsulated in tantalum. Values for increasing pressure only, but corrected for friction. Proposed hystereses (dotted lines) for 3°–5°C/sec rate and true equilibrium boundaries (solid line) for pure uranium.

Effects of Alloying

As may be ascertained from a scrutiny of Figs. 1 and 2, the transformation temperatures in uranium are *depressed* by capsule contamination in the following sequence:

$$\alpha\text{–}\beta: \quad BN > W > Cu > Mo,\ Ag > Ta;$$
$$\beta\text{–}\gamma: \quad BN,\ W > Cu,\ Ag,\ Mo > Ta;$$
$$\alpha\text{–}\gamma: \quad W > Ag > Ta.$$

This behavior is not readily explicable from an examination of the equilibrium phase diagrams.[10] The U-BN system is apparently not available and the Rough–Bauer[10] compilation contains little information concerning the effect of boron or nitrogen on the transformation temperatures in uranium. Recent work by Blumenthal[11] indicates that only a very slight lowering should occur due to carbon, assuming reaction of diamond. Likewise, little reaction with wolfram has been reported.[10] There is no published evidence of appreciable solubility of copper in uranium.[10] Silver is reported to have little effect on the transformation temperatures.[10] In U-Mo alloys, the γ phase is stabilized to lower temperatures and solubilities in β and α may be of the order of an atomic percent.[10] The maximum solubility of tantalum in uranium is less than 2 at.%.[10] In view of the unsatisfactory correlations between the reported equilibrium phase relations and the data at hand, the following mechanisms are proposed.

The contamination of the uranium is progressive, as shown by the continuing drop in transformation temperatures on successive cycles. Thus, one is led to inquire into the rates of diffusion of the encapsulating material into uranium sample. No work concerning the diffusion of dilute solutes in α- and β-uranium has been

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[10] F. A. Rough and A. A. Bauer, *Constitutional Diagrams of Uranium and Thorium Alloys* (Addison-Wesley Publishing Company, Inc., Cambridge, 1958).

[11] B. Blumenthal, J. Nucl. Mater. 2, 197 (1960).

found in the literature. However, Mossé et al.[12] have studied the diffusion of several elements into γ-uranium and find that the diffusion coefficient decreases with increasing Goldschmidt radius of the solute atom. For the present experimental geometry, reasonable parameters may be taken as $D \sim 10^{-6}$ cm²/sec at 850°C, $t \sim 5 \times 10^2$ sec, with the assumptions of perfect contact between uranium and container and no diminution of the diffusion rate under pressure. An overestimate of the depth of penetration of the solute is then calculated as about 1/10 the diameter of the cylinder. Since only a few atomic percent of solute might well cause the lowering of the transformation temperatures as observed, this could be accounted for by the diffusion processes herein outlined. There seems to be, in fact, a rough correlation between the amount of contamination, as indicated by the relative depressions of the transformation temperature, and the Goldschmidt radius of the solute atoms—in the approximate sequence C, B, N···Cu, Mo, W, Ag, Ta. Rothman[13] has studied the diffusion of gold in γ-uranium and finds a larger activation energy than that for self-diffusion; he also questions the results of Mossé et al.[12] Thus the situation appears to be rather confused. The present experiments suggest that the primary contamination is in β-uranium, since the α–β transformation temperatures show more lowering than the β–γ, α–γ boundaries. Little appears to be known about the diffusion rates of various elements in β-uranium; self-diffusion rates in β-uranium, though, are known[14] to be considerably smaller than in γ-uranium.

The α-γ Transformation

The direct α–γ transformation is studied here for the first time in relatively pure uranium. This transition does not have as large a hysteresis associated with it as do the α–β and β–γ transitions at the given rate of temperature change. This may imply that the α–γ transformation may be characterized as diffusionless, in contrast to the nucleation and growth features usually emphasized for the well-studied α–β and β–γ transformations. The slope of the α–γ phase boundary decreases with increasing contamination and this is probably related to the greater interdiffusion into γ-uranium.

Jayaraman et al.,[7] have attempted to draw an analogy between the high pressure Ga II–Ga III transformation and the α–γ uranium transformation. This attempted analogy was based on the identification of Ga II with the α-uranium-like metastable form of gallium studied by Defrain[15] and also on the speculative proposal[7] of a body-centered cubic structure for Ga III. If these suggestions are indeed valid and the Ga II–Ga III and α–γ uranium transitions are closely related, it may be possible to learn much about uranium by studying gallium since the temperature range is more convenient and the contamination problems less severe.

In order to explain the extensive stability field of Ga II, Jayaraman, et al.[7] also suggested that the α-uranium-like structure postulated for Ga II might continuously distort under pressure toward a hexagonal close-packed structure. High-pressure diffraction data and/or elastic moduli measurements are completely lacking for Ga II. However, this hypothesis of continuous distortion towards closest packing may be examined for α-uranium, which exists to ~100 kbar[3] despite the rather large (25%) volume change.[3]

The single crystal dilatometric measurements of Lloyd,[16] various polycrystalline x-ray diffraction studies,[1,16] and determinations[17] of the positional parameter y indicate some distortion toward a hexagonal close-packed structure at higher temperatures, but this tendency is hardly considered as pronounced. On the other hand, the 25°C elastic moduli[18] suggest a deformation with pressure more toward the "sheets" of atoms envisioned by Friedel.[19] Linear extrapolation of the elastic moduli data[18] from below 25°C to higher temperatures is not especially permissible in view of the complexity of the atomic interactions in the α-uranium structure; nevertheless, such extrapolations of the individual compliances, when made, do not support the hypothesis of distortion toward hexagonal closest packing. If the approximation of Friedel[19] is indeed more nearly realized upon compression and the covalent nature of the bonding more fully emphasized, it is difficult to understand the rather large decrease in resistance[4] and change in volume.[3]

Other Transformations

Duwez[20] has detected a transformation ("the X transformation") at temperatures between the α–β and β–γ transformations in uranium. Blumenthal[2] could not verify this β-phase anomaly in his careful experiments, however. At the beginning of these experiments, it was thought that the X transformation might be related, via a metastable extrapolation of the α–γ phase boundary, to the transformation phenomena occurring at high pressures, akin to that elucidated in the gallium investigation.[7] No intermediate thermal arrests were detected in the present experiments but this may have been because of the small heat involved and/or the relatively low rates of heating and cooling in the present experiments.

[12] M. Mossé, V. Lévy, and Y. Adda, Compt. Rend. 250, 3171 (1960).
[13] S. J. Rothman, J. Nucl. Mater. 3, 77 (1961).
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[15] H. Curien, A. Rimsky, and A. Defrain, Bull. Soc. Franc. Mineral. Crist. 84, 260 (1961).

[16] L. T. Lloyd, J. Nucl. Mater. 3, 67 (1961).
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[18] H. J. McSkimin and E. S. Fisher, J. Appl. Phys. 31, 1627 (1960).
[19] J. Friedel, J. Phys. Chem. Solids 1, 175 (1956).
[20] P. Duwez, J. Appl. Phys. 24, 152 (1953).

Fisher and McSkimin[21] have pointed out the existence of some sort of higher order phase transition in uranium at $42°\pm1°$K, based on anomalies noted in the thermal expansion, Hall coefficient, electrical resistivity, and thermoelectric power. Furthermore, the transition apparently is characterized by both an inflection point in the entropy vs temperature curve and by a vanishing thermal expansion coefficient.[22] It is thus not clear what the course of the transition at higher

pressures might be and, in fact, it may be that measurements of dT/dP might be a fruitful approach in determining the order of this transition.

ACKNOWLEDGMENTS

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[22] C. S. Barrett, M. H. Mueller, and R. L. Hitterman, Phys. Rev. **129**, 625 (1963).

Nuclear Spin-Lattice Relaxation in Noncubic or Imperfect Cubic Crystals for $I = 7/2$ or $9/2$

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Detailed calculations of the relaxational behavior of the central resonance line corresponding to transitions between levels $m = \pm\frac{1}{2}$ have been made for $I = \frac{7}{2}$ and $I = \frac{9}{2}$ in noncubic or imperfect cubic crystals. The behavior of the central line depends on the relative values of W_1/W_2 and differs considerably in the two special cases which have been considered.

RECENTLY, the relaxation behavior of the central line corresponding to transitions between levels $m = \pm\frac{1}{2}$ for $I = \frac{3}{2}$ and $\frac{5}{2}$ has been studied by Andrew and Tunstall[1] in imperfect cubic crystals and in noncubic crystals. The two special cases which they have considered are (1) when a strong saturating radio-frequency field is applied to the nuclear spin system which is in equilibrium with the lattice in the presence of an external magnetic field, and (2) when the external field is suddenly applied to the system which is in equilibrium in zero magnetic field. In the present paper we have examined the similar situation for $I = \frac{7}{2}$ and $\frac{9}{2}$.

QUADRUPOLAR RELAXATION FOR $I = 7/2$

Figure 1 shows the quadrupolar nuclear transitions for the case $I = \frac{7}{2}$. The differential equations governing the difference in populations of the levels for $I = \frac{7}{2}$ are given by

$$\dot{N}_3 = -\frac{1}{3}(6W_1 + W_2)N_3 + \frac{8}{21}(2W_1 + W_2)N_2$$
$$+ \frac{5}{7}W_2N_1 - \frac{2}{21}(8W_2 - 13W_1)n_0,$$

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[1] E. R. Andrew and D. P. Tunstall, Proc. Phys. Soc. (London) **78**, 1 (1961).

$$\dot{N}_2 = \frac{1}{3}(3W_1 - W_2)N_3 - \frac{2}{21}(16W_1 + 11W_2)N_2$$
$$+ \frac{5}{21}(W_1 + W_2)N_1 + \frac{20}{21}W_2N_0 + \frac{2}{21}(3W_1 + 2W_2)n_0,$$

$$\tag{1}$$

$$\dot{N}_1 = \frac{1}{3}W_2N_3 + \frac{8}{21}(2W_1 - W_2)N_2 - \frac{5}{21}(2W_1 + 7W_2)N_1$$
$$+ \frac{20}{21}W_2N_{-1} - \frac{2}{21}(3W_1 - 8W_2)n_0,$$

$$\dot{N}_0 = \frac{5}{7}W_2N_2 + \frac{5}{7}(W_1 - W_2)N_1 - \frac{40}{21}W_2N_0$$
$$+ \frac{5}{7}(W_1 - W_2)N_{-1} + \frac{5}{7}W_2N_{-2} - \frac{10}{21}(W_1 - 2W_2)n_0,$$

where $N_{m+\frac{1}{2}} = N_{m+1} - N_m$ ($m = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}, \pm\frac{7}{2}$) and $n_0 = N_{m+1} - N_m$ when no radio-frequency field is applied.

Writing $N_p' = N_p - n_0$, $N_{-1} = N_1$, $N_{-2} = N_2$, and $N_{-3} = N_3$, we obtain the following four equations:

$$\dot{N}_3' = -\frac{1}{3}(6W_1 + W_2)N_3' + \frac{8}{21}(2W_1 + W_2)N_2' + \frac{5}{7}W_2N_1',$$