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ACKNOWLEDGMENTS

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Low-Temperature Elastic Properties of ZrC and TiC

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The elastic constants of zirconium carbide and titanium carbide were determined over the temperature range of 4.2° to 298°K using a pulsed-ultrasonic phase comparison technique, and are compared to previously determined values for uranium carbide. Since these carbides are of the NaCl structure, only three independent constants are required to describe their elastic behavior. Their values at 298°K are

	ZrC _{0.94}	TiC _{0.91}
C_{11}	4.720 ± 0.005	5.145 ± 0.005
C_{12}	0.987 ± 0.005	1.060 ± 0.002
C_{44}	1.593 ± 0.002	1.788 ± 0.002

all in units of 10^{12} dyn/cm². The differences in the elastic behavior of these group IV, transition metal carbides and the monocarbide of uranium are discussed in reference to their different electronic structure.

I. INTRODUCTION

PREVIOUSLY determined low-temperature elastic constant data for stoichiometric single-crystal UC indicated two principal departures from the behavior typical of most materials.^{1,2} First, there was an increasing lattice instability as the temperature was lowered from room temperature. This instability was reflected by a decrease in the resistance of the lattice to a shear deformation across {100} planes at lower temperatures, the shear constant C_{44} decreasing by about 2% between 300° and 4.2°K. Second, the normal dependence of the elastic constants on the fourth power of the temperature at low temperatures was overtaken by a relatively strong contribution by the Fermi electrons to this dependence which enters as the square of the temperature. According to a theory explaining this behavior proposed by Bernstein,³ the magnitude and the algebraic sign of this effect depend upon the electronic density of states at the Fermi level and the shape of the Fermi surface.

ZrC and TiC are both group IV, transition metal carbides having the same sodium chloride structure as

UC.⁴ Their electronic structure is quite different from UC, however. A qualitative correlation between the superconducting critical temperature and electronic density of states at the Fermi level for transition metal carbides and nitrides of the NaCl structure has been proposed by Toth and co-workers,⁵ who also pointed out that the carbides and nitrides of U and Th are exceptions. It is the purpose of this work to study the elastic behavior of ZrC and TiC in contrast to that for UC published previously by the same authors.^{1,2}

II. SAMPLES

Several single crystals of both TiC and ZrC about 1–2 in. long by $\frac{1}{4}$ in. in diameter were obtained from Arthur D. Little, Inc. They were grown by the electron-beam floating-zone method, and were of slightly different chemical compositions and crystallographic orientations. The TiC crystal selected from these for the present work was of the composition TiC_{0.91}, and contained as impurities 50 ppm Ca, 10 ppm each of Be, Mg, K, Cr,

¹ L. J. Graham, H. Nadler, and R. Chang, *J. Appl. Phys.* **34**, 1572 (1963).

² L. J. Graham and R. Chang, *Compounds of Interest in Nuclear Reactor Technology*, J. T. Waber, P. Chiotti, and W. N. Miner, Eds. (AIME, New York, 1964), pp. 409–422.

³ B. T. Bernstein, *Phys. Rev.* **132**, 50 (1963); **137**, A1404 (1965).

⁴ In the text the formulas UC, TiC, ZrC imply nearly stoichiometric compounds of unspecified chemical composition, while the formulas TiC_{0.91}, ZrC_{0.94}, ZrC_{0.89} represent well-characterized compounds with carbon/metal atom ratios of 0.91, 0.94, and 0.89, respectively.

⁵ L. E. Toth, E. Rudy, J. Johnston, and E. R. Parker, *J. Phys. Chem. Solids* **26**, 517 (1965).

Ba, and Ta, and 1 ppm each of Si, Cu, Ag, and Bi. No porosity or second phases were observed metallographically. Its density was 4.905 g/cm³ calculated from the lattice parameter of 4.3290 Å.⁶ The crystal rod axis was 14° from [110] and 33° from [100], and the crystal was long enough to cut one sample of each of these orientations from it with the sample lengths along the acoustic path being 0.30600 and 0.30828 in., respectively.

The ZrC crystal used was of the composition ZrC_{0.94} containing as impurities 50 ppm Ti and 1 ppm each of Mg, Al, Si, and Fe, and with no porosity or second phase observable. The lattice parameter of ZrC goes through a maximum on the substoichiometric side of the phase diagram at about 45.5 at.% carbon,⁷ unlike that of TiC which is nearly constant in this range.⁶ Since the lattice parameter of ZrC is sensitive to composition in this range, it was measured for the sample and was found to be 4.6994 Å from which a density of 6.606 g/cm³ was calculated. This crystal rod axis was 20° from [100] and 30° from [110], but the crystal was only long enough to get one [100] oriented sample from it having a length of 0.29968 in. Since at least one other wave velocity must be measured in addition to those obtainable using a [100] oriented crystal, a second specimen having [110] orientation was prepared from another ZrC rod whose axis was 20° from [110] and 36° from [100]. This sample was of the composition ZrC_{0.89} and contained as impurities 1500 ppm N, 10 ppm Fe, and 1 ppm each of Mg, Al, Si, Ca, and Ti. There was no second phase apparent in its microstructure, but it contained a few microscopic, spherical pores in the center of the rod extending over its length. The lattice parameter of this sample was measured as 4.7004 Å from which a single-crystal density of 6.602 g/cm³ was calculated. The relationship between lattice parameter and composition for the two ZrC samples of this study agrees with that given by Sara.⁷ The difference in the elastic constants found for these two samples is discussed in a following section.

III. EXPERIMENTAL METHOD

A sensitive phase comparison technique using pulsed ultrasonics was used to determine the absolute values of the elastic wave velocities and their temperature dependence in the samples studied. Specifically, the length of the applied rf pulse was increased until successive echoes in the pulse-echo train overlapped. The radio frequency was then adjusted near a resonance frequency of the transducer until the overlapping echoes were exactly out of phase. At this condition the wave velocity bears a simple relationship to the applied radio frequency which can be measured with high precision. Accuracies of 0.1% in the absolute values of the wave velocities and a few parts in 10⁴ in their change with temperature are easily attainable using this method even

with small samples. A complete description of the method and an analysis of the errors involved has been reported previously.² The only change made in the procedure was that a gated cw source was used to supply the rf pulse rather than a pulsed oscillator. This made the measurement of the radio frequency easier.

Quartz transducers, $\frac{1}{8}$ in. in diameter, were bonded to the samples using Nonaq, and below 110°K, 2.5M centistoke DC-200 Dow-Corning silicone oil. X-cut and AC-cut transducers of 16-Mc/sec fundamental frequency were used to generate longitudinal and shear waves in the samples. Temperature measurements were made over the entire temperature range using a Au+2.1% Co vs Cu thermocouple and a sensitive micropotentiometer and galvanometer.

IV. RESULTS

The results of the room-temperature measurements for the four crystals studied are summarized in Table I. For a given sample in the table all the values in parentheses are calculated from the directly measured quantities (no parentheses) except for C' for the [100] samples which were calculated from the measured value of C' for the [110] samples assuming the same anisotropy parameter for both samples of a given carbide. This was necessary in the case of ZrC in order to obtain what is considered a more reliable value for C_{12} than was obtained from the direct measurements on the poorer quality [110] sample. For the TiC samples, however, the calculation of C' for the [100] sample in this manner was only to check the self-consistency of the measurements.

It is seen in Table I that the data for the two TiC samples cut from the same single crystal agree within 0.1%, while for the two different ZrC crystals the results differ by about 1%. This is outside of the experimental uncertainty and is attributed to the difference in sample characteristics. The different composition of the two samples could be the cause (ZrC_{0.94} and ZrC_{0.89}), but it could also be due to the porosity observed in the sample having the lower carbon content. The effect of this latter factor is difficult to evaluate because of the sample geometry.

The room-temperature values of the elastic constants of ZrC and TiC obtained here along with their estimated uncertainties are compared with values obtained by other investigators in Table II.⁸⁻¹⁰ Also shown are the elastic constants of UC. A reason for the large disagreement between our values and some of the published values for both TiC and ZrC cannot be given since details of the previous measurements are not available. Our values for TiC, however, agree with those reported by Bernstein⁸ and by Gilman and Roberts⁹ within

⁶ P. Costa and R. R. Conte, Ref. 2, pp. 1-27.

⁷ R. V. Sara, J. Am. Ceram. Soc. 48, 243 (1965).

⁸ B. T. Bernstein, unpublished; see also Ref. 22.

⁹ J. J. Gilman and B. W. Roberts, J. Appl. Phys. 32, 1405 (1961).

¹⁰ J. deKlerk, Rev. Sci. Instr. 36, 1540 (1965).

TABLE I. Elastic parameters determined at 298°K for ZrC and TiC. The quantities in parentheses are calculated from the other directly measured quantities for a given sample except for C' for the [100] crystals. All in units of 10^{12} dyn/cm² except for A which is dimensionless.

	ZrC _{0.94} [100] x-tal	ZrC _{0.89} [110] x-tal	(%) Diff.	TiC _{0.91} [100] x-tal	TiC _{0.91} [110] x-tal	(%) Diff.
$C_L = C_{11}$	4.7195	(4.6819)	-0.8	5.1428	(5.1477)	+0.10
$C = C_{44}$	1.5930	1.5727	-1.3	1.7869	1.7885	+0.10
C_{12}	(0.9871)	(0.9971)	+1.0	(1.0592)	(1.0605)	+0.12
$C' = \frac{C_{11} - C_{12}}{2}$	(1.8662) ^a	1.8424	-1.3	(2.0418) ^a	2.0436	+0.09
$C'_L = \frac{C_{11} + C_{12} + 2C_{44}}{2}$	(4.4463)	4.4122	-0.8	(4.8879)	4.8926	+0.10
$B = \frac{C_{11} + 2C_{12}}{3}$	(2.2312)	(2.2254)	-0.3	(2.4204)	(2.4229)	+0.10
$A = \frac{2C_{44}}{C_{11} - C_{12}}$	(0.8536)	(0.8536)	0	(0.8752)	(0.8752)	0

^a Calculated assuming A constant for both the ZrC and TiC specimens.

the uncertainty of conventional pulsed-ultrasonic techniques.

In Table III are shown the isotropic elastic constants calculated as an average of the Reuss and the Voigt approximations. Also shown are the values of the Debye temperature at 0°K calculated by the method of Anderson.¹¹

The temperature dependence of the elastic constants of ZrC and TiC are compared with that of UC in Figs.

TABLE II. Elastic constants of ZrC and TiC measured at 298°K compared with UC and with the results of previous work. All in units of 10^{12} dyn/cm².

	C_{11}	C_{12}	C_{44}
ZrC	4.720 ± 0.005^a	0.987 ± 0.005	1.593 ± 0.002
ZrC	4.280^b	0.408	1.464
TiC	5.145 ± 0.005^a	1.060 ± 0.002	1.788 ± 0.002
	5.245^b	0.980	1.809
	5.00^c	1.13	1.75
	3.891^d	0.433	2.032
UC	3.184 ± 0.004^e	0.862 ± 0.003	0.656 ± 0.001

^a Present work. ^d Reference 10.

^b Reference 8. ^e Reference 2.

^c Reference 9.

TABLE III. Polycrystalline isotropic elastic constants at 298°K calculated as an average of the Reuss and the Voigt approximations. The Debye temperatures were calculated from the 0°K values of the elastic constants.

	TiC	ZrC	UC
E , Young's modulus, 10^6 psi	65.14	58.92	30.76
G , shear modulus, 10^6 psi	27.34	24.61	11.98
K , bulk modulus, 10^6 psi	35.13	32.36	23.73
ν , Poisson's ratio	0.1908	0.1966	0.284
θ_0 , Debye temperature, (°K)	946.3	713.8	330.0

¹¹ O. L. Anderson, J. Phys. Chem. Solids **24**, 909 (1963).

1-4. The original data were taken at 2°-5°K intervals over the temperature range of 4.2°-298°K, defining smooth curves over this range, and then a correction for thermal expansion was applied, resulting in the curves shown in these figures. Figure 5 shows the thermal expansion corrections that were used. The dependence of the elastic constants on thermal expansion enters as a length squared times the density, or as L^{-1} . Linear thermal expansion data for the carbides are available for temperatures above 300°K. In Fig. 5 we have extrapolated these data to 0°K using the known data for Fe and Ti as a guide. The correction to the elastic constants at 0°K is about 0.1%, so if the extrapolation is in error by as much as 20%, the error in the elastic constants is not too significant.

In addition to the temperature dependences shown in Figs. 1-4, the temperature dependence of C'_L was

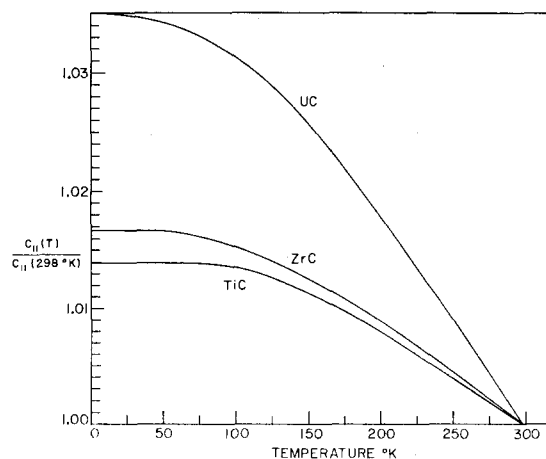


FIG. 1. Relative values of C_{11} with temperature.

also measured for TiC. This produced a redundancy in the measurements allowing two independent ways of determining the temperature dependence of C_{12} . These are shown in Fig. 6, where the upper dashed curve for TiC was determined from $C_{12} = C_L - 2C'$ and the lower dashed curve from $C_{12} = C'_L - C' - C$. The solid curve for TiC is the same as in Fig. 2 and is considered to be the best representation of the temperature dependence of C_{12} . The maximum deviation of about 0.2% of the dashed curves from the smoothed curve would result from about an 0.02% error in the primary data. This error could be due to interference in the measurements caused by reflections from the sides of the small samples used, or to a change in the characteristics of the transducer bond with temperature, since the measurements were made slightly off the resonant frequency of the transducer.

It is apparent that even greater accuracies than are commonly achieved using ultrasonic techniques are required in determining the temperature dependence of C_{12} . This accuracy would be desired, for example, in determining the temperature dependence of the bulk

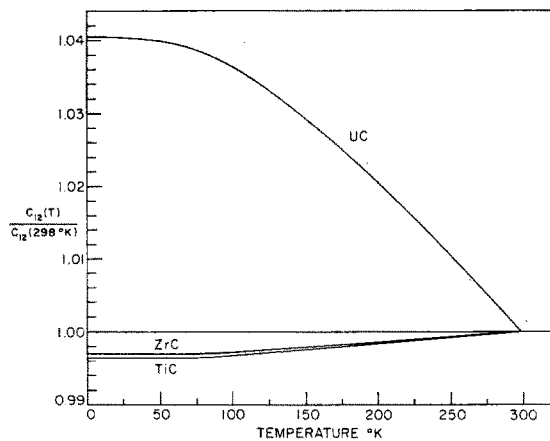


FIG. 2. Relative values of C_{12} with temperature.

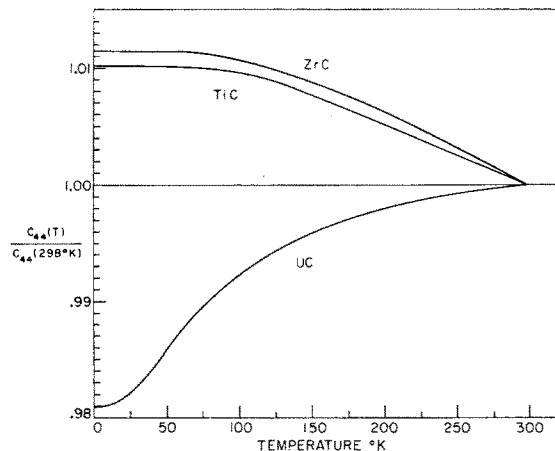


FIG. 3. Relative values of C_{44} with temperature.

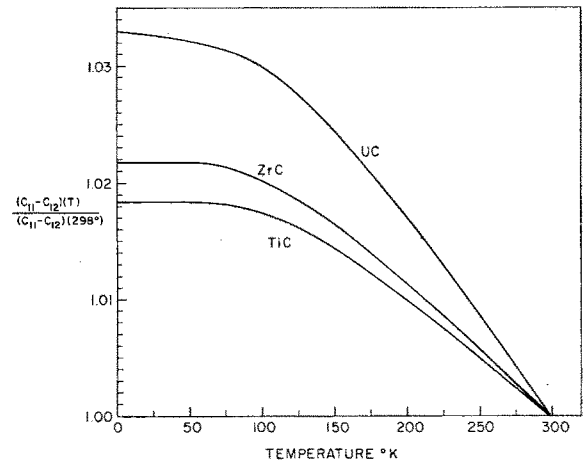


FIG. 4. Relative values of $(C_{11} - C_{12})/2$ with temperature.

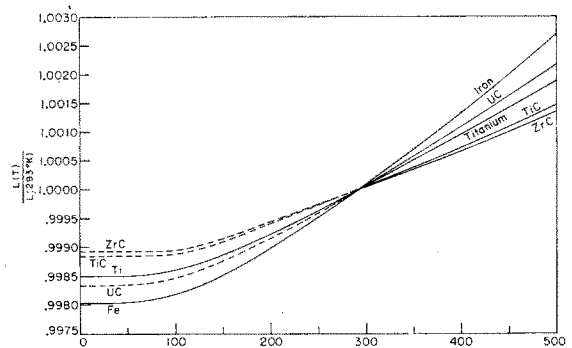


FIG. 5. Thermal expansion correction which was applied to the data.

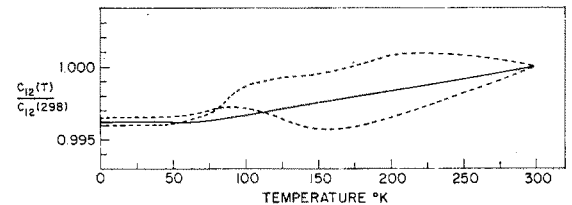


FIG. 6. Uncertainties involved in the temperature dependence of C_{12} for TiC. The dashed lines are the result of two independent determinations as described in the text. The solid line is considered the best estimate of the temperature dependence.

modulus from the relation $K = (C_{11} + 2C_{12})/3$. When this dependence is needed, it may even prove necessary to measure the temperature dependence of the compressibility directly.

The temperature dependence of C_{12} for ZrC shown in Fig. 2 resulted from the temperature dependences of C_L and C' determined for the two different samples. The maximum deviation of the data from the smoothed curve shown in this figure was 0.02% of C_{12} . While the absolute values of the elastic constants for the two ZrC samples differed by about 1%, it was assumed that their temperature dependences would be the same. This as-

sumption may not be strictly valid, but the result obtained appears reasonable.

V. DISCUSSION OF RESULTS

It can be seen in Table I and in Figs. 1–4 that the elastic constants and their temperature dependence for ZrC and TiC are very similar. A comparison of these with the elastic behavior of UC, however, shows several marked differences. First, the two unusual features in the elastic behavior of UC mentioned in the introduction were not observed for the two group IV carbides of this study. That the T^2 dependence of the elastic constants at low temperature was not seen is in agreement with the low value of the electronic density of states at the Fermi level which for TiC has been found from specific heat and magnetic susceptibility measurements to be about 0.5 electrons/atom/eV.⁶ The value for ZrC is probably about the same, so the electronic contribution to the temperature dependence of the elastic constants in these materials should be too small to be experimentally detected.³

Alers and Waldorf were the first to see the T^2 dependence of the elastic constants at low temperatures experimentally in their study of vanadium, niobium, and lead.¹² In other materials such as copper and aluminum, where the density of states is low, the effect is not seen. The magnitude of the effect observed for UC, which has a density of states of 4.3 electrons/atom/eV, was nearly the same as that seen previously for vanadium (3.9 electrons/atom/eV; c.f. 0.32 for copper).

The second unusual feature in the elastic behavior of UC, the positive temperature coefficient for the shear constant C_{44} , was also not observed for the carbides of the present study. In fact UC seems to be unique in this respect. Other materials for which a positive temperature coefficient of an elastic constant has been observed all behave differently in some way from UC. Off-stoichiometric CuZn (β -brass)¹³ and fused silica¹⁴ show a positive temperature coefficient over a wide range of temperature which for β -brass has been associated with the order-disorder phenomenon. All of the elastic moduli of V_3Si decrease with decreasing temperature, the shear modulus $(C_{11}-C_{12})/2$ essentially vanishing at a low temperature.¹⁵ This increasing lattice instability at low temperatures is associated with a structural transformation which occurs below 22°K. In niobium, the shear constant C_{44} has a minimum at about 200°C, increasing about 10% to a maximum at about 1000°C before decreasing again with increasing temperature.¹⁶ No explanation for this behavior has been offered.

The positive temperature coefficient of C_{44} for UC,

which points out a decreasing ability of the lattice to resist a shear deformation across {100} planes at lower temperatures, suggests a tendency to squeeze out the carbon atom that lies between two <100> oriented uranium atoms.¹⁷ This may imply an unusually strong metal-metal bond which increases in effectiveness at lower temperatures where the amplitude of lattice vibration is diminished. The elastic constants of ZrC and TiC, on the other hand, are seen in Fig. 3 to be normal in their temperature dependence, since the lattice becomes "stiffer" at lower temperatures for these materials as is the case for almost all crystalline solids.

Another difference in the elastic behavior of the carbides studied here compared to that of UC occurs in the "Poisson constant" C_{12} . The large, negative temperature dependence of this constant for UC is like that of silicon and germanium,¹⁴ whereas the small, positive dependence for the other carbides is similar to that of some of the alkali halides¹⁸ and bcc transition metals.¹⁹ Also, the deviation from the Cauchy equality, $C_{12}-C_{44}=0$, is in the opposite sense for ZrC and TiC than it is for UC. de Launay²⁰ has shown that in the "free electron gas" approximation for fcc and bcc metals the deviation from the Cauchy equality is just the bulk modulus of the electron gas, i.e., $C_{12}-C_{44}=K_e$. The equation given by de Launay for K_e based on this model is

$$K_e \cong 2\pi \left(\frac{\pi}{3}\right)^{\frac{1}{3}} \left(\frac{\hbar^2}{2m^*}\right) (N_a n_0)^{\frac{1}{3}},$$

where N_a is the number of atoms/cm³, n_0 is the number of "free" electrons/atom, and m^* is the effective mass of the "free" electrons. Applying this equation to UC, taking $n_0 \cong 1$ free electron per uranium atom and $m^* \cong m$, results in $K_e = 0.13 \times 10^{12}$ dyn/cm² compared with $C_{12}-C_{44} = 0.21 \times 10^{12}$ dyn/cm². The agreement is rather good, but may also be fortuitous. Piper²¹ found only about 0.08 free electrons per metal atom in TiC and therefore K_e would be expected to be much smaller (about 10^{10} dyn/cm² for this material and also probably for ZrC). It was found in the present study, however, that both ZrC and TiC have negative values for $C_{12}-C_{44}$. These results may indicate that the "free electron model" applies better to UC than to the other carbides. Other crystals for which qualitative agreement has been found are Cu,²⁰ and V, Nb, Ta, Mo, and W.²² However, Cr (which exhibits antiferromagnetism below 310°K), the diamond structure crystals, diamond, Ge,

¹⁷ We are indebted to H. B. Huntington who suggested this as a possible explanation of the observed behavior of the anomalous temperature dependence of the shear constant C_{44} for UC.

¹⁸ J. K. Galt, Phys. Rev. **73**, 1460 (1948); W. C. Overton, Jr., *ibid.* **84**, 758 (1951); R. Dalven and C. W. Garland, J. Chem. Phys. **30**, 346 (1959).

¹⁹ D. I. Bolef and J. de Klerk, J. Appl. Phys. **33**, 2311 (1962); F. H. Featherston and J. R. Neighbors, Phys. Rev. **130**, 1324 (1963); K. J. Carroll, J. Appl. Phys. **36**, 3689 (1965).

²⁰ J. de Launay, J. Chem. Phys. **21**, 1975 (1953).

²¹ J. Piper, J. Appl. Phys. **33**, 2394 (1962).

²² W. S. Williams and R. G. Lye, AD 449222, Wright-Patterson Air Force Base, Ohio (15 September 1963), pp. 31–33.

¹² G. A. Alers and D. L. Waldorf, Phys. Rev. Letters **6**, 677 (1961).

¹³ G. M. McManus, Phys. Rev. **129**, 2004 (1963).

¹⁴ H. J. McSkimin, J. Appl. Phys. **24**, 988 (1953).

¹⁵ L. R. Testardi *et al.*, Phys. Rev. Letters **15**, 250 (1965).

¹⁶ P. E. Armstrong and H. L. Brown, paper presented at ASM meeting, Detroit, 20 October 1965.

and Si, and certain ionic crystals such as LiF and MgO all have negative values of $C_{12}-C_{44}$,²² as do TiC and ZrC.

VI. CONCLUSIONS

Several points of difference between the elastic behavior of the group IV transition metal carbides, ZrC and TiC, and UC have been discussed, all of which deal with the electronic structure of these carbides. There has been some success in the past in applying the band structures calculated for the transition metals to their carbides in correlating some of their physical properties.²³ Only recently, however, has there been an attempt

²³ See for example H. Bilz, *Z. Physik.* **153**, 338 (1958); L. Kaufman, *Trans. Met. Soc. AIME* **224**, 1006 (1962); E. Dempsey, *Phil. Mag.* **8**, 285 (1963).

to calculate the band structures for the heavy metals, uranium, neptunium, and plutonium, and their carbides.²⁴ It is hoped that physical property data such as presented here will be an aid in furthering that work.

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²⁴ E. A. Kmetko, *Bull. Am. Phys. Soc.* **10**, 1192 (1965).

The Metastable Solid-Liquid Phase Boundary

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The solid-liquid interface of a material which is transforming under transport-controlled conditions is examined from the point of view of stability. Three forms of interfaces, namely the spontaneously unstable, the metastable, and the stable, appear to be possible. The metastable form of solid-liquid interface has not, as yet, been considered, apparently because its presence has not been recognized. As is shown, however, it can be predicted by the perturbation analysis of interface stability and examples of its occurrence in crystal growth are examined.

I. INTRODUCTION

THIS work proposes the existence of a dynamic metastable form of solid-liquid interface and relates this mode of solidification to two other forms of moving interfaces, i.e., the unstable interface and the stable interface.

For simplicity, the discussion is restricted mainly to a single planar interface and the various forms which this interface can adopt. The reasoning applies generally, however, to all interface shapes and may well hold for transformations other than the solid-liquid example treated here.

Early theories of planar interface stability were based upon the development of constitutional supercooling.¹⁻³ At the onset of this condition, the interface was assumed to break down from a planar morphology to a cellular form, in which caps of solid projected into the constitutionally undercooled zone. The rate of interface advance in the examples considered was always constrained by a positive temperature gradient in the liquid

ahead of the interface and, in general, the theory agreed well with the experimental results. The existence of a stable planar interface in the presence of a negative liquid temperature gradient, however, was not considered. A more recent treatment of interface stability by Mullins and Sekerka⁴ employed an analysis based on the stability of an infinitely small amplitude perturbation δ . If $d\delta/dt$ is found to be positive, the interface is assumed to be unstable and vice versa. This criterion of stability inherently makes use of the principle that a faster growing interface is more stable, since $d\delta/dt$ is simply the time derivative of amplitude or distance. Analysis of a planar interface by this means is very general and can be used for pure or impure melts in which the interface is constrained or unconstrained. Unlike the older constitutional undercooling criterion, the temperature gradient in the liquid ahead of the interface may be negative. The possible existence of this negative temperature gradient ahead of a planar interface stimulated the present work, which consequently makes extensive use of the Mullins and Sekerka analysis.⁴

¹ J. W. Rutter and B. Chalmers, *Can. J. Phys.* **31**, 15 (1953).

² W. A. Tiller, K. A. Jackson, J. W. Rutter, and B. Chalmers, *Acta Met.* **1**, 428 (1953).

³ W. A. Tiller and J. W. Rutter, *Can. J. Phys.* **34**, 96 (1956).

⁴ W. W. Mullins and R. F. Sekerka, *J. Appl. Phys.* **35**, 44 (1964).