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Activation Volumes for Self-Diffusion in Ordered AuZn Alloys*

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Measurements have been made to 5.2 kbar at 541 °C of the simultaneous diffusion of Au^{195} and Zn^{65} in ordered AuZn alloys having nominal compositions of 49.0-, 50.0-, and 51.2-at.% Zn. The activation volumes ΔV obtained from these data are maximum at 50 : 50 composition and decrease on both sides of stoichiometry. The value of ΔV at 50 : 50 is approximately 8.5 ± 0.8 cm^3/mole or 0.9 times the molar volume V_M, which is of the correct magnitude for a vacancy mechanism. The activation volumes for the two constituents are equal to within the experimental accuracy. The results are discussed in terms of the correlated six-jump vacancy mechanism operative in these highly ordered alloys, and are related to vacancy-defect *vis-à-vis* antistructure-defect structures at off-stoichiometric compositions.

I. INTRODUCTION

Atomic diffusion in metals occurs primarily by a vacancy mechanism, wherein thermally activated lattice vacancies exchange positions with the constituent atoms, giving rise to mass transport.[1] In binary metallic alloys of the *AB* type and having the CsCl structure, each atom is surrounded by eight nearest-neighbor atoms of the opposite species. Diffusion in such systems also proceeds via a vacancy mechanism but involves a highly correlated motion which preserves the degree of long-range order. All evidence, both experimental and theoretical, seems to indicate that this mechanism consists of a sequence of six jumps or atom-vacancy exchanges around a planar or folded rhombus.[2–9]

In a recent study of the temperature and composition dependence of self-diffusion in highly ordered AuZn alloys,[10] it was concluded that a vacancy-defect structure exists on the gold sublattice in the Zn-rich alloys. This excess vacancy concentration results from the need of the lattice to accommodate the excess concentration of Zn atoms while at the same time maintaining long-range order. On the Au-rich side, however, an antistructural type of defect was found, with the excess Au atoms spilling onto the Zn sublattice. The evidence came largely from the observed composition dependence of the activation energy ΔH (or Q), and frequency factor $D_0(=\gamma a^2 \nu f e^{\Delta S/R})$, the decrease in both quantities being more precipitous on the Zn-rich side. Since the activation energy and volume, ΔH and ΔV, are interrelated parameters, it may be expected that activation-volume measurements should reveal a similar behavior.

The activation volume is given by[11,12]

$$\Delta V = \left(\frac{\partial \Delta G}{\partial P}\right)_T \tag{1}$$

$$= -RT\left(\frac{\partial \ln D}{\partial P}\right)_T + RT\gamma_G \kappa_T \ . \tag{2}$$

Also,

$$\Delta V = \Delta V_f + \Delta V_m \ . \tag{3}$$

Here γ_G is the Grüneisen constant, κ_T is the isothermal compressibility, and ΔV_f and ΔV_m are the activation volumes of formation and motion, respectively. At the 50 : 50 composition all vacancies are thermally activated (intrinsic) vacancies, requiring energies of both formation and motion. For the case where a large nonequilibrium concentration of vacancies exists due to nonstoichiometry (extrinsic vacancies), much of the transport will be via such vacancies. Hence the energy required for an atom to make a diffusion jump is less. The effective activation volume will then be given by

$$\Delta V_{\text{eff}} = q\Delta V_f + \Delta V_m \ , \tag{4}$$

where q is the ratio of the number of intrinsic vacancies to the total number of vacancies present. Thus, when all vacancies are thermally activated (intrinsic), $q = 1$ and Eq. (3) is obtained; when all are extrinsic, $q \to 0$ and $\Delta V_{\text{eff}} \simeq \Delta V_m$.

It was decided, therefore, to make diffusion measurements as a function of pressure also, in order to determine the activation volumes in AuZn as a function of composition. This additional information should further elucidate the mechanism or mechanisms for diffusion in such ordered-alloy systems. Indeed, this is the first reported measurement of activation volumes in ordered CsCl-type metallic alloys. AuZn alloys remain highly ordered up to the melting point and do not exhibit any solid-state transformation at elevated temperatures and pressures and hence presented no experimental difficulties. For full appreciation of this investigation it is recommended that Ref. 10 should be read along with this paper.

II. EXPERIMENTAL PROCEDURES

The AuZn single-crystal specimens used in this work were grown and prepared by the methods described in Ref. 10. The specimens were polished and annealed, and the Au^{195} and Zn^{65} tracers were electroplated on. A polished-alloy cap (cut from the adjoining part of the single-crystal ingot) was then pressure welded to the specimen by heating under uniaxial pressure, for a time sufficient to obtain a diffusion weld but short compared to the eventual diffusion time. The weld time was included as part of the "warm-up" correction. The purpose of the cap was to prevent any loss of Zn due to evaporation at the diffusion temperatures.

Alloys of nominal 49.0, 50.0, and 51.2-at.%-Zn composition were used; the precise compositions are listed in Table I.[13] The high-pressure diffusion anneals were carried out in an internally heated pressure vessel using Ar gas (99.995% pure) as the pressure medium.[14] The actual temperatures of the runs were normalized to 541.1 °C using the previously determined composition-dependent activation energies.[10] A correction of

TABLE I. Pressure and composition dependence of self-diffusion coefficients in β'-AuZn at 541.1 °C (values in parentheses are interpolations to the nominal composition).

Composition (at.% Zn)	Pressure (kbar)	D_{Zn} (cm^2/sec) (±5%)	D_{Au} (cm^2/sec) (±5%)	D_{Zn}/D_{Au}
		49.0-at.% Zn (nominal)		
49.09[a]	0	4.31×10^{-10} (4.20)	4.84×10^{-10} (4.95)	0.89
48.63	3.10	3.69×10^{-10} (3.67)	4.53×10^{-10} (3.72)	0.81
49.06	4.10	3.64×10^{-10} (3.64)	4.29×10^{-10} (4.45)	0.85
48.98	5.24	3.11×10^{-10} (3.11)	3.90×10^{-10} (3.85)	0.81
		50.0-at.% Zn (nominal)		
50.12[a]	0	6.42×10^{-10} (5.60)	4.34×10^{-10} (4.00)	1.48
50.12	1.60	5.55×10^{-10} (4.70)	3.60×10^{-10} (3.18)	1.55
49.85	3.10	3.49×10^{-10} (3.46)	2.34×10^{-10} (2.18)	1.51
49.97	5.24	3.09×10^{-10} (3.09)	2.05×10^{-10} (2.01)	1.51
		51.2-at.% Zn (nominal)		
51.84[a]	0	4.70×10^{-9} (2.3)	1.46×10^{-9} (0.93)	2.23
51.33	1.60	3.16×10^{-9} (2.60)	1.18×10^{-9} (1.03)	2.68
51.08	3.10	1.92×10^{-9} (2.30)	8.31×10^{-10} (9.70)	2.33
51.24	5.24	1.88×10^{-9} (1.78)	7.57×10^{-10} (7.25)	2.46

[a] From Ref. 10.

0.5 °C/kbar to the temperature measured on the Pt/Pt10-at.%Rh thermocouple was also made.[14–16] The thermocouple junction was placed in close contact with the cap end of the specimen, near the welded interface. The temperature during each run was maintained constant to within ±1 °C. Pressure was measured on a precision Heise gauge.

The standard procedures of serial sectioning with a precision lathe were used to measure the penetration of the radioisotopes. The weight of each section, the diameter, and the measured density were used to determine the penetration. Simultaneous counting of the Zn^{65} and Au^{195} tracer activities was accomplished using a two-channel scintillation counter with energy discrimination set in each channel to detect one of the tracers. A correction was made for interference of Zn^{65} (1.1-Mev γ) in the Au^{195} (0.067-Mev γ) channel. The diffusion coefficients were determined from a least-squares fit to the relation

$$c(x,t)=[c_0/(\pi D t)^{1/2}]\,e^{-x^2/4Dt}\,, \tag{5}$$

the solution to the diffusion equation for the planar-source boundary conditions. This relation was obeyed over a range of specific activity of two decades or more in all cases. The ratio of the diffusion coefficients was determined directly from the measured ratio of tracer activities, following the relation

$$\ln(c_{Au}/c_{Zn}) = \text{const} + (1 - D_{Zn}/D_{Au})\,x^2/4D_{Zn}t\,. \tag{6}$$

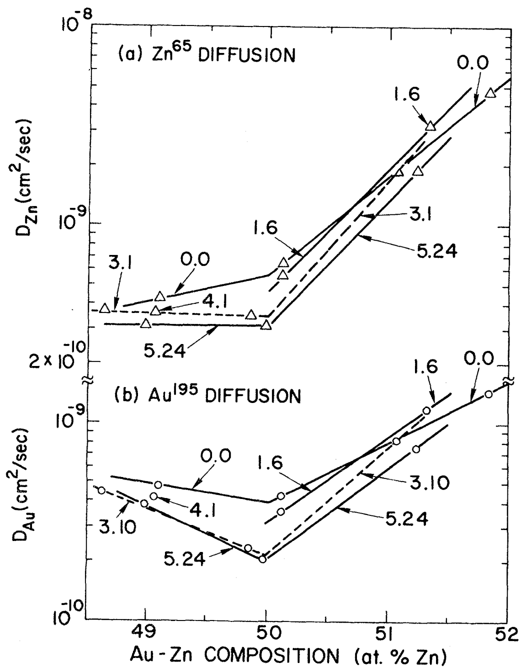

FIG. 1. Pressure and composition dependence of diffusion coefficients of (a) Zn^{65} and (b) Au^{195} in β'-AuZn. Zero-pressure data from Ref. 10. Numbers with arrows indicate pressure in kbar.

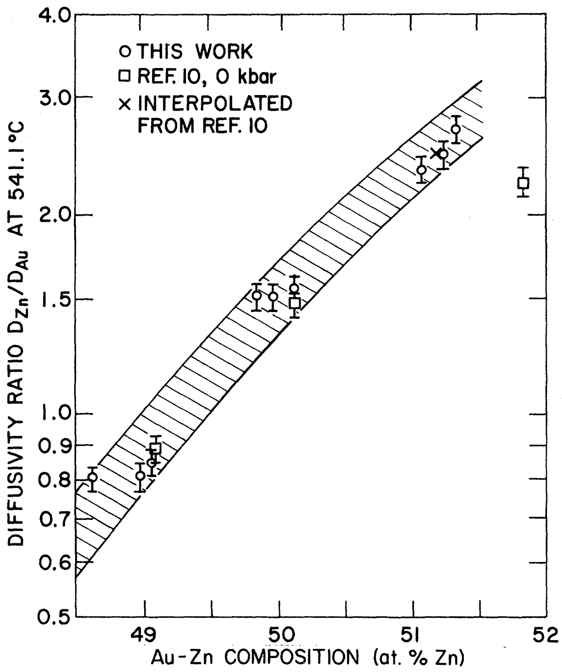

FIG. 2. Pressure and composition dependence of the directly measured ratio D_{Zn}/D_{Au}.

III. RESULTS

The results of the high-pressure diffusion runs are summarized in Table I and displayed as a function of composition and pressure in Fig. 1. The diffusivity ratios D_{Zn}/D_{Au}, calculated directly from Eq. (6), are plotted as a function of composition in Fig. 2. Some composition variation was encountered about each of the nominal compositions, but its effect was most pronounced in the Zn-rich alloys because of the high sensitivity of the diffusivities to composition in that region. This is seen most dramatically in Fig. 2, where, for example, the 0-kbar point (from Ref. 10) at 51.84-at.% Zn and the 3.1-kbar point at 48.63-at.%-Zn composition fall well away from the mean of the neighboring points. In fact, the former point was so far separated from the other points near 51.2% that values for D_{Zn} and D_{Au} had to be interpolated from Fig. 3 of Ref. 10. The corresponding ratio of interpolated D's is shown as the "x" in Fig. 2. The ratios D_{Zn}/D_{Au} were found generally to fall within a band, as shown in Fig. 2, which is ±5% from the mean at each composition. The ratios were independent of pressure to within the limits of experimental error.

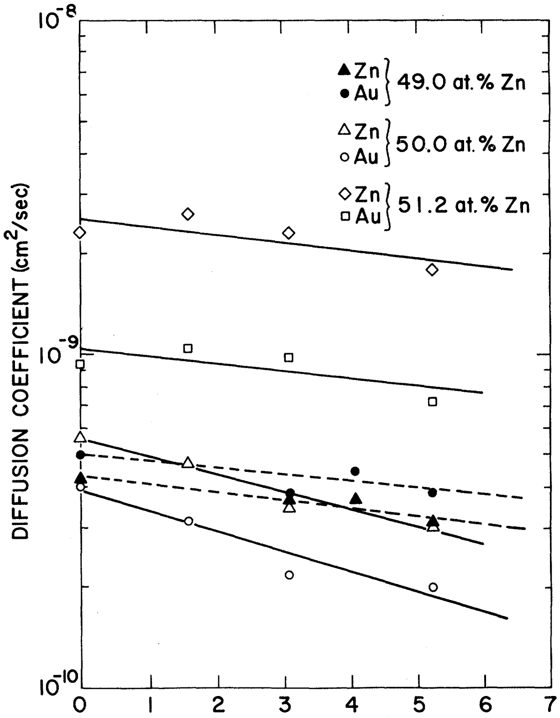

FIG. 3. Pressure variation of the diffusion coefficients in 49.0-, 50.0-, and 51.2-at.%-Zn alloys.

In order to estimate the activation volumes, the data were normalized to the compositions 49.0-, 50.0-, and 51.2-at.% Zn. The corresponding plots of $\ln D$ vs P are given in Fig. 3. The activation volumes computed from the slopes of these lines are given in Table II and plotted as a function of composition in Fig. 4. Despite the large uncertainty in the 0-kbar points at 51.2-at.%-Zn composition and the 3.1-kbar-Au point at 49% alluded to earlier, those points were included in the calculations of ΔV. The correction term in Eq. (2) containing the Grüneisen constant has not been included because it turned out to be considerably smaller than the uncertainty in the first term.

The apparently sizable composition variation for the various samples obtained from each single-crystal ingot is probably the single greatest source of error or uncertainty in these results. Other errors, such as uncertainty in diffusion temperature, correction for welding time, sectioning and counting errors, and the limited pressure range, all contribute to the total uncertainty of the measured D values of perhaps 5%. The stated uncertainties in ΔV given in Table II are simply the root-mean-square values obtained from the least-squares fits but reflect the uncertainty in D.

TABLE II. Activation volumes for self-diffusion in β'-AuZn.

Composition (at.% Zn)	ΔV-Zn^{65} (cm^3/mole)	ΔV-Au^{195} (cm^3/mole)	ΔV_{av}[a] (cm^3/mole)	$\Delta V_{av}/V_M$[b]
49.0	3.5±0.6	2.8±1.4	3.4±0.6	0.36
50.0	8.1±1.0	9.4±1.5	8.5±0.8	0.90
51.2	3.7±1.6	3.4±1.6	3.5±1.1	0.37

[a] Weighted average. [b] $V_M = 9.45$ cm^3/mole.

IV. DISCUSSION

The results of the present measurements show that the activation volumes for diffusion in ordered AuZn are a maximum at about 50:50 composition and decrease rapidly on either side of stoichiometry. Also, the values of ΔV for diffusion of Zn^{65} and Au^{195} tracers are equal, to within the experimental uncertainty, as may be seen from Table I and Fig. 2, where the ratio D_{Zn}/D_{Au} is seen to be nearly independent of pressure for any given composition.

Despite the limitations in the data, the general trend is clear even from Fig. 1, where it is evident that D is suppressed most rapidly with pressure at the 50:50 composition and less rapidly in off-stoichiometric alloys. At the maximum, ΔV is approximately 8.5 ± 0.8 cm^3/mole or 0.9 times the molar volume V_M, and is of the correct magnitude for a vacancy diffusion mechanism.

Because of the specialized techniques involved in conducting high-pressure, high-temperature diffusion experiments, activation volumes have been measured in a comparatively small number

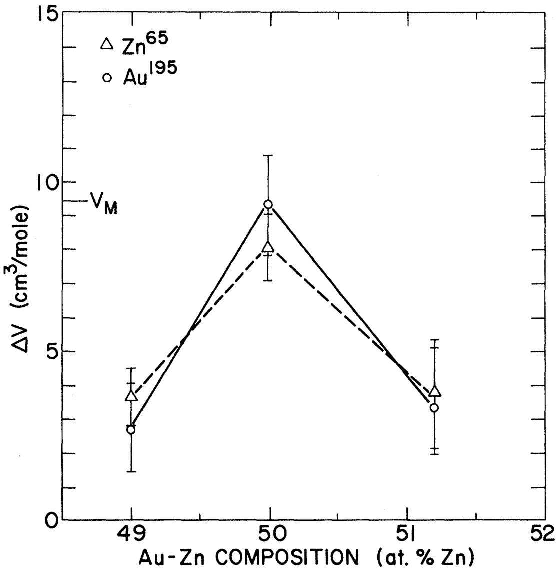

FIG. 4. Composition variation of the activation volumes. The molar volume, 9.45 cm^3/mole, is shown for comparison.

TABLE III. Activation-volume measurements in metallic alloy systems.

System	Structure	Method	$\Delta V/V_M$	Ref.
α-AgZn	fcc	anelastic relaxation	0.54	23
FeV	bcc	chemical diffusion	0.45–0.60	24
Ag-Au	fcc	self-diffusion	0.73	25
α-FeCo	bcc (disordered)	self-diffusion	0.6	26
β'-AuZn	bcc (ordered)	self-diffusion	0.3–0.9	This work

of materials. Summaries of the experimental results reported prior to 1970 may be found in Refs. 11 and 17. In general, pure fcc metals are found to have activation volumes typically in the range 0.65–0.90 times the molar volume V_M, and bcc metals in the range 0.4–0.6 V_M. Notable exceptions are Al[18] and Na,[19] respectively. Of hcp metals reported, Be has $\Delta V/V_M = 1.2$,[20] Zn = 0.43,[21] and Cd = 0.58.[22]

In metal-alloy systems the few measurements that have been reported are summarized in Table III. The results in all of these alloy systems generally conform to the pattern that a homogeneous, concentrated, disordered alloy has an activation volume for diffusion which is an average of the values of the constituent pure metals of the same crystal structure. In α-AgZn,[23] the value of $\Delta V/V_M$ is smaller than that of pure Ag (0.90), but intermediate between Ag and Zn. In Fe-V,[24] the value decreased for increasing vanadium concentration, presumably because of the greater relaxation allowed by the smaller vanadium atoms in the Fe lattice. AgAu[25] and FeCo[26] appeared virtually indentical to the corresponding pure metals. On this account, a disordered AuZn bcc alloy, if it were to exist, would be expected to have a value of $\Delta V/V_M$ of approximately 0.5 for vacancy diffusion. Among the measured $\Delta V/V_M$ values in AuZn alloys listed in Table II, the ones for the 50-at.%-Zn alloy are considerably larger; the other alloys seem to be more what is expected. This large discrepancy needs examination.

Although activation volumes have been measured in no other ordered metallic systems with which comparisons may be made, measurements have been made in alkali halides, where the order is almost perfect. For a series of alkali halides, Yoon *et al.*[27] reported values of the formation volume $\Delta V_f/V_M$ ranging from 1.1 to 1.8. These values may be slightly too large if there is a significant anion contribution to the electrical conductivity, but such a correction is thought to be small. This large formation volume is attributed to outward relaxation of the nearest-neighbor ions around a vacancy due to Coulomb repulsion of the like-charged ions. While the origin of the ordering energy in metallic alloys may not contain as significant a contribution from the Coulombic forces as in alkali halides, nevertheless, *AB* alloys have been considered in this way with some success using a screened charge distribution around the ions.[28] Comparing activation volumes in ordered AuZn and alkali halides should then be at least qualitatively valid. The observation of a large activation volume in the 50:50-AuZn alloy, in particular, may then be attributed to a comparatively large formation volume caused by the repulsion of (like-charged) ions neighboring about the vacancy. Indirect evidence for the tendency toward outward dilatation indicated here is seen from lattice-parameter measurements made on FeCo, in which the room-temperature lattice parameter was found to be increased by the presence of quenched-in long-range order.[29]

In the present measurements of activation volumes in ordered AuZn alloys, an exceptionally large value of the long-range order (LRO) parameter[30] ($S = 0.96$ in 50-at.%-Zn alloy at 650 °C, which is only 75 °C below its melting point) gives an added factor of considerable importance. To preserve this high degree of LRO, the diffusion mechanism requires a highly correlated vacancy motion consisting of six successive atom-vacancy jumps; the first three jumps create local disorder and the following three restore the order. The model permits the net diffusion of atoms of both the species in the alloy, but with an increased activation energy determined to a large extent by a term ΔH_{0j}, defined as the local disordering component of the activation enthalpy required to bring a vacancy to the third position of the six-jump cycle. Values of ΔH_{0j} have been computed for β'-AgMg alloys[4] and turn out to be sizable fractions of the diffusion activation energy. In off-stoichiometric alloys, a vacancy may find itself a first or second neighbor to a "wrong" atom, thus partly or wholly obviating the need of the six-jump cycle. Consequently the contribution of the ΔH_{0j} may be lowered from the values for movement of the vacancy in the case of perfect order. A similar behavior of the $p\Delta V_j$ contributions to the Gibbs free-energy variation over the six-jump cycle could also be conceived of, with the expected result being that the measured activation volume in off-stoichiometric alloys will be lower than that at 50:50 composition, and may be lower than the disordered value ($\Delta V/V_M \leq 0.5$). The observed values of ΔV in 49.0- and 51.2-at.%-Zn alloys of about 3.5 cm^3/mole ($\Delta V/V_M \simeq 0.37$) are consistent with this picture and with the other bcc metals and alloys.

In the off-stoichiometric ordered alloys, two situations are possible. Either (i) the excess atoms may spill over and occupy substitutional positions on the wrong sublattice (antistructure defects), or (ii) the excess atoms may be compensated for by vacancies being created on the other sublattice (extrinsic vacancies). Previous work on this and related alloy systems[4,5,10] have indicated that antistructure defects [No. (i)] dominate in the noble-metal-rich alloys, and vacancy defects in the Zn-rich alloys. On the Au-rich side, the presence of the antistructure defects should lead to a gentle lowering of ΔV for the reasons discussed above. This is seen in the case of the 49.0-at.%-Zn alloy in Fig. 4, although the trend is only qualitative.

In the Zn-rich alloys one also expects a decrease in the activation volumes owing to the presence of a vacancy-defect structure, in accordance with Eq. (4) for $q<1$. The drop in this case is expected to be even more precipitous than seen in Fig. 4 for the 49.0-at.% alloy. However, no such sharp drop is seen in Fig. 4 for the 51.2-at.% alloy; in fact the plot is roughly symmetrical. This observation may suggest an absence of a vacancy defect structure in the 51.2-at.%-Zn alloy. On the other hand, it is not easy to dismiss the earlier results indicating the existence of a vacancy-defect structure in β'-AuCd[5] and β'-AuZn[10] in the Cd- and Zn-rich alloys. In those experiments, the diffusion coefficient D was made to range over a factor of 100 by varying the temperature, whereas a factor of 2 was the largest change observed due to pressure. The precision in determining the activation energies and preexponential factors is therefore obviously greater than that possible in determining the activation volumes. Hence, while the apparent symmetry of Fig. 4 may seem to suggest that the same mechanism is operative on both sides of stoichiometry, the percentage uncertainties in ΔV are too large to safely conclude that and discount the temperature results.

This study leaves many questions unanswered, such as the relative contributions to the activation volumes from the different ionic radii for Au and Zn (1.37 and 0.74 Å, respectively) or the metallic radii[31] (1.44 and 1.38 Å, respectively); the influence of reduced local order, when antistructure defects are present, on the formation volume; whether ΔV (or ΔH) should saturate to ΔV_m (or ΔH_m) when sufficiently off the stoichiometric composition on the Zn-rich side (corresponding to $q \to 0$); or if the formation and/or motion volumes of vacancies on the two sublattices are equal.

The present work has, nevertheless, shown that diffusion in the AuZn alloys takes place by a vacancy mechanism and that the activation volumes are maximum in the 50:50 alloy and fall off on either side of the stoichiometry. The data seem to suggest that the vacancy-defect structure in Zn-rich alloys may not be as dominant as previously thought, but that antistructure defects may also play a sizable role in these alloys as well as in the noble-metal-rich alloys.

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Lattice Dynamics of YZn

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Phonon dispersion curves for YZn along the $(0, 0, \zeta)$, $(\zeta, \zeta, 0)$, (ζ, ζ, ζ), and $(\frac{1}{2}, \frac{1}{2}, \zeta)$ directions have been measured by inelastic neutron scattering at room temperature. A sixth-neighbor force-constant model was used to obtain a fit to the data; there is residual indication of weak forces of still longer range. The frequency distribution function, Debye temperature as a function of temperature, and mean-square atomic displacements were calculated from the model. No Kohn-type anomaly was observed, and YZn was not found to become superconducting down to 1.2 K. Comparison of the dispersion curves of YZn with those of β-brass shows some pronounced differences, though there is a coincidence of accidental degeneracy between the transverse acoustical and transverse optical branches in both materials at $(0, 0, \frac{1}{2})$.

I. INTRODUCTION

The elucidation of phonon dispersion curves and vibrational spectra from inelastic-neutron-scattering (INS) measurements has been done for a number of materials, but relatively little work has been done on metallic materials involving both lattices with bases and two different atomic species. The first such study was of β-brass (formula CuZn with the cubic CsCl-type structure) by Gilat and Dolling.[1] In the case of β-brass, the over-all shapes of the dispersion curves were found to be quite similar to those which would be expected for a simple bcc element. Because of the small mass difference between copper and zinc atoms, only two of the theoretically expected splittings between the acoustical and optical branches of the dispersion curves at the Brillouin-zone boundaries were large enough to be observed. The present investigation was undertaken to look further at another CsCl-type structure. Initial attention was given to the phase[2] AuZn which is congruently melting at 725 °C. The valence-electron configuration in gold should be closely analogous to that in copper and the primary difference between AuZn and CuZn was expected to be the mass difference between gold and copper. A suitable single crystal of AuZn was grown, and an ultrasonic technique was used for the determination of the elastic constants.[3] Some initial neutron scattering data were accumulated, but it soon became apparent that the absorptivity of AuZn for neutrons was more severe than anticipated. As a result, the requisite time at the neutron flux levels of the presently available reactor was considered too costly to justify the accumulation of sufficient data for a complete delineation of the dispersion curves.

An alternative material had, therefore, to be selected, and the phase YZn was chosen. This phase also crystallizes[4] with the CsCl-type structure. Selection of YZn as the test material sacrificed the advantageous similarity in valence-electron configuration that exists between AuZn and CuZn, but retention of zinc as the second component did at least maintain a common factor. The dominant consideration in the selection of YZn was the favorable ratio that was indicated between neutron scattering and neutron absorption. Thermal neutron cross sections have been tabulated[5] for yttrium as 1.28 ± 0.02 b for absorption, 7.60 ± 0.06 b for coherent scattering, and 0.05 ± 0.03 b for incoherent scattering, and for zinc as 1.1 ± 0.04 b for absorption and 4.1 ± 0.1 b for coherent scattering. The neutron cross sections are colligative, so the favorable scattering-to-absorption ratios for the elements are also characteristic of