dicate a quadratic dependence on ω.

By taking differences between the curve fits for the liquid-rotating and disk-rotating cases as before, the heavy lines result as shown. The essential feature here is that we obtain nearly a single straight line through the origin, thus indicating a quadratic dependence on ω for the vortex contribution but with the unusual feature of a sign change in response at the origin.

Based on this analysis we deduce a vortex-induced torque law of the form

$$\tau = A\,\omega\,|\omega|, \tag{2}$$

where our best (average) value for A at this temperature is 2.7×10^{-5} dyn cm/(rpm)^2, or 2.4×10^{-3} dyn cm sec^2/rad^2. Preliminary, rough estimates of such torque based on density of vortex lines, angular momentum content, and deposition rate yield order-of-magnitude agreement with this value.

In summary, we believe that the vortex-deposition model is in good basic agreement with our measurements, which constitutes to our knowledge the first evidence of a macroscopic vortex-probe interaction. By taking suitable differences between liquid-rotating (vortices present) and disk-rotating (vortices absent) cases we are able to present measurements of the temperature and speed dependence of the vortex-induced torque.

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[1] Product of Millipore Corp., Bedford, Mass. 01730.

[2] J. R. Pellam, Phys. Rev. Lett. 5, 189 (1960).

[3] W. J. Trela, Phys. Rev. Lett. 29, 38 (1972).

[4] R. F. Lynch and J. R. Pellam, Phys. Rev. Lett. 31, 17 (1973).

[5] An early, partial report of this work may be found in R. F. Lynch and J. R. Pellam, in *Proceedings of the Fourteenth International Conference on Low Temperature Physics, Helsinki, Finland, 1975* (North-Holland, Amsterdam, 1975), p. 203.

[6] Some of the data to be presented no doubt contain new information on the anomaly, but in this note we prefer to focus on the novel effect.

[7] Presumably, even if the anomaly did not exist, the same general conclusions could have been drawn (from a porous-disk experiment). We hope to simulate this situation by the use of symmetrical (porous) objects such as cylinders or spheres, whose behavior will not be affected by the anomaly.

[8] J. R. Pellam, in *Proceedings of the Seventh International Conference on Low Temperature Physics, Toronto, Canada, 1960* (Univ. of Toronto Press, Toronto, 1961), p. 446.

[9] J. R. Pellam, Phys. Rev. Lett. 27, 88 (1971).

[10] W. König, Ann. Phys. (Leipzig) 43, 51 (1891); L. L. Beranek, *Acoustic Measurements* (Wiley, New York, 1949), p. 148.

[11] A further case was investigated with the 5-μm material: The equilibrium position of the disk was rotated through 90°. We found essentially a near inversion of the deflection–rotation-sense asymmetry.

[12] The word destroyed is not intended in a literal sense; we envision some process whereby the angular-momentum content of the vortex is deposited on the disk. Detailed understanding of such momentum absorption is properly the subject of further investigation.

[13] We assume angular corrections to D are small, and were therefore neglected.

Phase Stability in Transition-Metal Laves Phases

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We report a successful first-principles calculation of the correlation between crystal structure and d-electron–to–atom ratio in the transition-metal Laves alloys. The existence of a Hume-Rothery–type rule is related to geometrical similarities of the structures. The d-band binding is the main determinant of structure, and the common-band model is well obeyed, with a deviation whose physical interpretation we discuss. An experimental test is suggested.

The celebrated Hume-Rothery–type rules, associating alloy phase stability with average electron concentration, are not yet understood theoretically in transition-metal alloys.[1] Two major questions arise. Firstly, what features are necessary to produce a correlation of the stability of phases with ranges of electron-to-atom ratio $\mathfrak{z}$?[2] Secondly, why is average $\mathfrak{z}$ a sufficient parameter, i.e. why can we use a common-band model, in which we neglect differences in the self-energies of the alloy components?[1] We will investigate the first question by calculating the relative stability of Laves alloys, which will demonstrate the importance of certain geometrical characteristics, and we will find a behavior nearly that of a common band, but with a small deviation, which we can interpret physically and to which we can assign a rough measure. These latter considerations form a preliminary basis for answering the second question above.

The Laves phases are a set of three related complex structures which occur frequently in AB_2 binary alloys,[3] and are isomorphs of $\mathrm{MgCu_2}$, $\mathrm{MgZn_2}$, and $\mathrm{MgNi_2}$. We here consider only alloys where both components are transition metals. Geometrical similarities are evident in the layer stacking[3] (Greek letters denoting A sites, Latin B, in the notation of Allen, Delavignette, and Amelin[4]: $\mathrm{MgCu_2}$ type, $\alpha A \alpha c \beta B \beta a \gamma C \gamma b \ldots$; $\mathrm{MgZn_2}$ type, $\alpha A \alpha c \beta B \beta c \ldots$; $\mathrm{MgNi_2}$ type, $\alpha A \alpha c \beta B \beta c \alpha A \alpha b \gamma C \gamma b \ldots$.

Transition-metal alloys exhibit regular structural trends between the three Laves phases with varying composition.[5,6] This has attracted a substantial amount of experimental and theoretical work,[5-9] but until now no first-principles calculation of electronic energy has been possible. We have computed d-band densities of states by the recursion method of Haydock, Heine, and Kelly,[10,11] the more conventional method via the band structure $E(\vec{k})$ being impractical because of the large number of atoms per unit cell. We thus make the usual assumption for transition metals, that the structural variation of d-electron binding dominates that of the sp band.[12,13]

We have adopted a model alloy Hamiltonian, for all three structures, in which there is no difference in site-diagonal energies for A and B components. However, off-diagonal terms effectively distinguish between the crystal potential around A and B sites in the following way: A linear-combination-of-atomic-orbitals interpolation-scheme Hamiltonian[14] was used, with the hopping integrals of Pettifor[15] for Ni throughout, i.e. the same for A-A, A-B, and B-B interactions. Now overlap parameters vary approximately with interatomic distance[15,16] as $1/r^5$, and, for a given value of r, are larger for the first three columns of the transition metals than for the next five.[13] The two effects tend to cancel because of the characteristic positions of the A and B components in the periodic table and the interatomic distances,[3] so that our model takes these effects into account approximately. The calculation is therefore properly termed a common-band model since it is slightly better than the rigid-band and virtual-crystal approximations. We ignore the sp band and its hybridization with the d band. We expect the hybridization effect to be sizable, but its variation with structure is a higher-order term which in any case is greatest at the lower end of the band,[13,17] fortunately the part of least practical interest for the Laves phases. The d-band densities of states per formula unit AB_2, $n(E)$, were derived from the Green's functions which are given by the recursion method in continued-fraction form, taken to fifteen levels in clusters of about 1500 atoms. Gaussian quadrature was used to calculate integrated quantities such as the number of d electrons per atom, $\mathfrak{z}$, and their total energy per atom, U, for a given Fermi level E_F:

$$\mathfrak{z}(E_\mathrm{F}) = \tfrac{1}{3}\int^{E_\mathrm{F}} n(E)\,dE\,, \tag{1}$$

$$U(E_\mathrm{F}) = \tfrac{1}{3}\int^{E_\mathrm{F}} E\,n(E)\,dE\,. \tag{2}$$

Thus U is obtained as a function of $\mathfrak{z}$. We shall always use $\mathfrak{z}$ in this restricted sense, applying only to the d band. Full details of these calculations will appear.[18] Of course the total energy should include various electrostatic, exchange, and correlation terms beside the sum of one-electron energies (2), but these are expected to be nearly identical for the three structures which for ideal c/a ratios have identical interatomic distances and densities, only differing in stacking sequence. This expectation is based on experience with sp-bonded metals where all the terms can be calculated in detail,[1] and on Pettifor's calculation of the fcc and hcp energy differences for transition metals.[19]

The total A-site d-band densities of states for the three structures are very similar, with a peak-to-peak correlation. The A-site density of states shows a fairly good division into bonding and antibonding states. The left-hand side of Fig. 1 shows the stable phase, i.e. the structure with the smallest ΔU, against $\mathfrak{z}$. Here ΔU refers to the energy of the $\mathrm{MgCu_2}$, $\mathrm{MgZn_2}$, or $\mathrm{MgNi_2}$ phase relative to the $\mathrm{MgCu_2}$ phase for the same $\mathfrak{z}$. The differences are of the order of 1 mRy, but the absolute value should only be taken as an approximate lower bound for real alloys, because of the overlap parameters used. In the region where alloys lie, about $\mathfrak{z} = 3$ to 8, we see that the most stable structures are firstly $\mathrm{MgCu_2}$ (from $\mathfrak{z} = 3.4$), then $\mathrm{MgZn_2}$ (from $\mathfrak{z} = 4.9$), next $\mathrm{MgNi_2}$ (around $\mathfrak{z} = 6.5$ up to 6.9), again $\mathrm{MgCu_2}$, and finally from $\mathfrak{z} = 7.7$, $\mathrm{MgNi_2}$. A notable feature of the curves is the cyclic variation, giving regions of

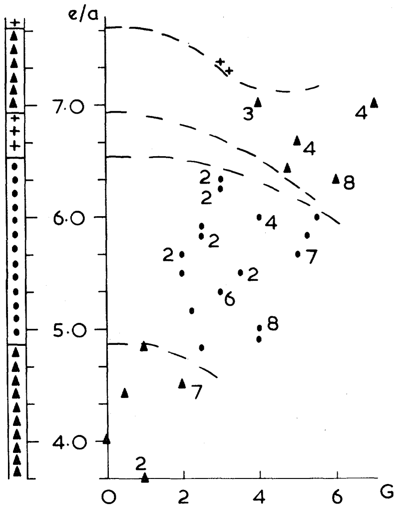

FIG. 1. Comparison between observed and calculated structures. Experimental alloy structures are plotted as a function of d-band filling per atom, e/a, and group-number difference G between components. ▲, $MgCu_2$ structure; ●, $MgZn_2$ structure; +, $MgNi_2$ structure. A data point representing more than one alloy has beside it the number represented. The column at the left indicates the theoretically most stable phase, and the dashed lines show putative phase boundaries, coinciding with theory at $G=0$.

stability associated with ranges of $\mathfrak{z}$; $\Delta U(MgCu_2 \rightarrow MgZn_2)$ has five zeros, and $\Delta U(MgCu_2 \rightarrow MgNi_2)$ six zeros between the endpoints. This behavior is a consequence of the similar layer stacking structures, which determine, via closed chains of neighboring atoms, the moments of the total density of states.[20] This consequence, that stacking similarities lead to a few regions of Hume-Rothery-type stability, should occur in many transition-metal alloys, not just the Laves phases. For example, we suggest that this is the reason for the success of the Engel-Brewer theory,[21] which may be connected with ours by regarding the *sp* part of the Brewer hybrid as a parameter correlated with our d-band $\mathfrak{z}$.

The justification for our model alloy must rest on agreement with experiment. Table I lists all the relevant compounds and structures taken from Sinha[3] and Nevitt,[22] excluding, on the basis of the original experimental reports, some six unclear cases, e.g., $MoFe_2$ whose structure is most likely intermediate between two Laves phases.[4,23] We also disregard ferromagnetic alloys, e.g., $ZrFe_2$, where up- and down-spin bands are filled unequally, leaving the 76 alloys of Table I. Each has to be assigned a $\mathfrak{z}$ (d electrons only) by subtracting some estimated number of *sp* electrons. The latter are estimated from available band-structure calculations for pure transition metals as follows, treating all three transition series alike: 1 *sp* electron for group-III to -V elements (Sc to V, etc.), $\frac{3}{4}$ *sp* electron for group VI (Cr, etc.), and $\frac{1}{2}$ for groups VII and beyond (Mn to Ni, etc.).

The 76 alloys are then plotted on the right of Fig. 1, the numbers in the diagram indicating the number of alloys falling on one point. The observed structures may be compared with the calculated ones on the left of the diagram. Of the 76 alloys, the structures of 60 are correctly accounted for by the theory without any adjustment. This result has been achieved without varying any optimizing parameters, and so indicates the general correctness of the model within the approximations of the theory.

We may conclude that the d-band binding in a common-band model is the major influence determining which of the three Laves phases is stable in a given alloy, contrary to some suggestions of

TABLE I. Low temperature structures of the transition-metal Laves phase alloys.

$MgZn_2$ structure										
$ScFe_2$	$ScMn_2$	$ScOs_2$	$ScRe_2$	$ScRu_2$	$ScTc_2$	YOs_2	YRe_2	YRu_2	YTc_2	LuFeCr
$LuMn_2$	$LuOs_2$	$LuRe_2$	$LuRu_2$	LuRhRu	$LuTc_2$	$TiFe_2$	$TiMn_2$	$ZrMn_2$	$ZrOs_2$	$LuRh_{0.5}Ru_{1.5}$
$ZrRe_2$	$ZrRu_2$	$ZrTc_2$	$HfMn_2$	$HfOs_2$	$HfRe_2$	VCoTa	VFeTi	VNbNi	VTaNi	NbCrNi
$NbFe_2$	$NbMn_2$	TaCrCo	TaTiCo	TaCrNi	$TaFe_2$	$TaMn_2$	HfVNi	ZrVNi		
$MgCu_2$ structure										
$ScNi_2$	YNi_2	YPt_2	$LuNi_2$	$TiCr_2$	$ZrCr_2$	$ZrMo_2$	ZrV_2	ZrW_2	$HfCr_2$	$HfMo_2$
HfV_2	HfW_2	$NbCo_2$	$TaCr_2$	TaFeNi	TaV_2	$TaCo_2$	$ScCo_2$	YCo_2	$LuCo_2$	$TaV_{1.5}Mn_{0.5}$
YRh_2	$LuRh_2$	$ScIr_2$	YIr_2	$LuIr_2$	$HfCo_2$	$ZrCo_2$	$TiCo_2$	$ZrIr_2$	$ZrV_{0.5}Ni_{1.5}$	
$MgNi_2$ structure										
$NbCo_3$	$Ta_{0.8}Co_{2.2}$									

other authors.[5,7,9] This is our main physical conclusion. It is contrary to a basic assumption of the Brewer-Engels theory[21] which has not been applied to the Laves phases but which for similar alloys relates structure to the number of *sp* electrons.

We may now semiempirically incorporate the major factor neglected so far, the site-diagonal energy differences. For simplicity we will work in terms of group-number difference, G, between the group numbers in the periodic table of the B- and A-site elements (averaged over A and over B sites for pseudobinaries):

$$G = G_B - G_A . \tag{3}$$

For this purpose we count the Co group as IX and the Ni group as X. It is clear from Fig. 1 that those alloys for which the theory fails have a high average G, and that the phase boundaries curve downwards from the theoretical values at $G = 0$. The sign of the curvature may be explained by the fact that in the region of $\mathfrak{z}$ of interest, the A site $n(E)$ is relatively flat and the trends in structure follow more the number of electrons on the B site, which for large G is larger than the mean $\mathfrak{z}$ plotted in Fig. 1. Moreover we expect any charge-transfer effects to vary as G^2, giving a parabolic behavior to the phase boundaries for small G (Fig. 1). We have carried out one calculation with the A and B sites having different diagonal energy which results in approximately 3.5 more electrons on the B site than the A site, i.e., it corresponds to $G \approx 3.5$ minus any charge transfer due to electronegativity effects. Interestingly, $n(E)$ on the A and B sites has very much the same structure as for $G = 0$, with the amplitude at the lower end of the band enhanced on the B site and reduced on the A site. The total $n(E)$ and phase-stability curves therefore look very much the same as for $G = 0$, which helps to explain the success of simple models based on counting the total number of electrons in a common band. There are of course small shifts. In the range $\mathfrak{z} = 6$ to 7 we find the calculated phase boundary between the $MgCu_2$ and $MgZn_2$ structures is shifted 0.8 electrons to lower $\mathfrak{z}$, which is of the correct sign and order of magnitude but about double the observed trend in the phase boundary (Fig. 1). We find the calculated phase boundary at $3.7 < \mathfrak{z} < 5$ has disappeared, the $MgZn_2$ phase being stable throughout the range. By interpolation we estimate the stability of the $MgCu_2$ phase to have maximum extent out to $G \approx 4$ at $\mathfrak{z} = 4.2$. The experimental data (Fig. 1) show the downward trend of the phase boundary but are insufficient for further comparison in this region.

We see from Fig. 1 that around $\mathfrak{z} = 6.7$, at $G = 0$, the calculations predict a region of stability for the $MgNi_2$ structure, but there are no experimental data. The radius-ratio constraint for Laves phases makes it doubtful that any would form at the lower-G part of the region, but at higher G an experimental test may be possible. For example, we would expect $TaFe_{1.75}Ni_{0.25}$, if it formed a Laves phase, to take the $MgNi_2$ structure.

Full details of our basic calculations, including applications to magnetic alloys and temperature allotropy, will appear.[24] We thank Mr. C. M. M. Nex for assistance with computer calculations.

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[1] V. Heine and D. Weaire, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 430 ff.

[2] M. H. Cohen, in *Alloying Behaviour and Effects in Concentrated Solid Solutions*, edited by T. B. Massalski (Gordon and Breach, New York, 1965), p. 11 ff.

[3] A. K. Sinha, Prog. Mater. Sci. 15, 79 (1972).

[4] C. W. Allen, P. Delavignette, and S. Amelincki, Phys. Status Solidi (a) 9, 237 (1972).

[5] R. P. Elliott and W. Rostoker, Trans. Am. Soc. Met. 50, 617 (1958).

[6] A. E. Dwight, Trans. Am. Soc. Met. 53, 479 (1961).

[7] R. L. Berry and G. V. Raynor, Acta Crystallogr. 6, 178 (1953).

[8] W. E. Wallace and R. S. Craig, in *Phase Stability in Metals and Alloys*, edited by P. S. Rudman, J. Stringer, and R. I. Jaffee (McGraw-Hill, New York, 1967), pp. 255–272.

[9] A. R. Edwards, Metall. Trans. 3, 1365 (1972).

[10] R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C 5, 2845 (1972), and 8, 2591 (1975).

[11] R. Haydock and M. J. Kelly, Surface Sci. 38, 139 (1973).

[12] J. Friedel, J. Phys. F 3, 785 (1973).

[13] F. Duscatelle and F. Cyrot-Lackmann, J. Phys. Chem. Solids 32, 285 (1971).

[14] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

[15] D. G. Pettifor, Ph.D. thesis, University of Cambridge, 1970 (unpublished).

[16] V. Heine, Phys. Rev. 153, 673 (1967).

[17] D. G. Pettifor, *Metallurgical Chemistry Symposium 1971* (National Physical Laboratory and Her Majesty's Stationery Office, London, 1972), pp. 191–199.

[18] R. Haydock and R. L. Johannes, to be published.

[19] D. G. Pettifor, J. Phys. C 3, 267 (1970).

[20] F. Cyrot-Lackman, Adv. Phys. 16, 393 (1967); J. Friedel, in *The Physics of Metals I,* edited by J. Ziman (Cambridge Univ. Press, Cambridge, England, 1969), p. 352, Ref. 10.

[21] W. Hume-Rothery, Prog. Mater. Sci. 13, 229 (1967).

[22] M. V. Nevitt, in *Electronic Structure and Alloy Chemistry of Transition Metals,* edited by P. A. Beck (Wiley, New York, 1963), p. 160.

[23] R. P. Elliott, Armour Research Foundation, Chicago, Technical Report No. 1, OSR-TN-247, 1954 (unpublished), p. 17.

[24] V. Heine and R. L. Johannes, to be published.

Chemisorption-Induced Surface Umklapp Processes in Angle-Resolved Synchrotron Photoemission from W(001)†

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Angle-resolved photoemission, using synchrotron radiation, from the chemisorption system W(001) +H shows a very large doublet of peaks at initial energies -1.3 and -0.6 eV for quarter-monolayer coverage which disappear at higher coverage. The emission lobes are strongly peaked in the ⟨110⟩ azimuths and are attributed to essentially pure bulk W transitions. The electrons are emitted in the new directions through the influence of "extra" surface reciprocal lattice vectors associated with the hydrogen $C(2\times2)$ superstructure.

The appearance of new peaks in photoemission spectra due to chemisorption of atoms or molecules is usually attributed to a modified density of initial states associated with the bonding of the chemisorbed species to the surface.[1] However, chemisorbed layers are known frequently to form ordered overlayers with a corresponding modification in the surface reciprocal lattice. Photoemission theory then implicitly allows the possibility of new emission peaks which we term "kinematic" because they appear solely as a consequence of the new set of reciprocal lattice vectors which may participate in the emission process. As a result, photoemission spectra, particularly angle-resolved spectra from chemisorbed layers, may show new peaks which bear no relation to a possible modified density of initial states. Any interpretation of such data must therefore take into account the possibility that observed structure might have such a purely kinematical origin.

We have observed a rather dramatic manifestation of such an effect in angle-resolved photoemission spectra for the chemisorption system W(001) + H_2. A very large doublet of peaks appears at around a quarter monolayer coverage and we present persuasive evidence that this structure is kinematic in character. We identify the doublet as being due to photoemission from essentially bulk W states into new directions as a result of an energy conserving umklapp process involving a new set of surface reciprocal lattice vectors formed by the ordered overlayer of hydrogen atoms.

The tungsten (001) sample was a thin ribbon and standard cleaning procedures were used. The base pressure was $\lesssim 2\times10^{-10}$ Torr. Synchrotron radiation from the storage ring at the University of Wisconsin at Stoughton in the photon energy range 10 eV $\lesssim h\nu \lesssim$ 26 eV was focused on the sample at normal incidence. The resultant s polarization suppresses certain large emission features associated with this system for p polarization.[2] Those features therefore were not present to complicate our observations. With use of a cylindrical mirror analyzer modified with a movable aperture restricting the emission to a 4° cone, angle-resolved energy distribution curves (AREDC's) were measured at azimuthal angle φ and polar angle θ which could be scanned over most of the emission hemisphere.[3] The angle φ was varied by rotating the sample about its surface normal, and we denote that angle by the direction, in the surface, contained in that azimuth, i.e., the ⟨110⟩ azimuth or $\varphi = \langle 110\rangle$. The relative hydrogen coverage is denoted by C and saturated coverage, $C=1$, is termed a monolayer of hydrogen atoms. A quarter monolayer is denoted by H($C/4$) where values of C were calculated using Madey's[4] results for the sticking co-