An approximate numerical integration[11] for the case where $E = 1.12\hbar\omega_L$, which is the harmonic localized mode energy for this model if $\mu' = 0.5 \mu$, yields the result that the integral in Eq. (47) is about 5×10^{-3}. For this case, then, we find

$$\Gamma/2 \approx 0.2\hbar\omega_L r^2. \tag{48}$$

Because of the fact that r is identified with the anharmonic interaction of an isolated impurity atom with its neighbors, it is difficult to make a numerical estimate for it. The usual parameter of anharmonicity, the Grüneisen constant,[12] is measured for interactions between atoms of the host crystal. But if we associate these quantities with each other, we find that a reasonable Grüneisen constant (of the order of unity) for a crystal implies that r for the force between each atom

and its nearest neighbors is of the order of 10^{-2}. Therefore, from Eq. (48) we see that the order of magnitude of the ratio of the half-width to energy of the anharmonic localized mode is 10^{-4}. Within the limitation of the calculations, this result is not in disagreement with the widths obtained in the references cited above.[6] No careful quantitative work will be done here, because we do not believe the model we use to be realistic enough to warrant it. The significance of the present work lies more in the form than in the magnitude of the answers.

The real part of $F(E)$ is just Eq. (45) with the integral replaced by a principal value integral. It will be of the same order-of-magnitude as the imaginary part; hence the shift of the localized mode (downward in energy for frequencies close to the phonon cutoff) is comparable to its width.

VI. ACKNOWLEDGMENT

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[11] An analytic approximation can be made in the limit of small impurity mass.
[12] See, for example, P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 1.

Energy Bands for the Iron Transition Series*

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Preliminary energy-band calculations for elements of the iron transition series have been completed using the augmented plane-wave method. The results include plots of energy as a function of wave vector along a line of symmetry for elements crystallizing in the face-centered cubic (Ar, Co, Ni, Cu), body-centered cubic (V, Cr, Fe), and hexagonal close packed (Ti, Zn) structures. These results indicate the presence of systematic trends in the band structures for the various elements and provide some justification for the application of the rigid band model to transition metals and their alloys.

I. INTRODUCTION

ENERGY bands have been calculated for a majority of the elements in the iron transition series using the augmented plane-wave (APW) method.[1,2] While the present results are preliminary in nature and not in any sense complete, they may be of some interest to experimentalists and theoreticians who are concerned with the electronic structure of the transition-series elements. The present results represent energy bands for three different crystal structures, with a variety of lattice constants. Despite the detailed differences that are imposed by symmetry requirements and variations in lattice constants, the results suggest some interesting and rather clear-cut trends in the band structure of these elements as one proceeds through the

transition series. These calculations lend some support to the rigid band model for the transition series. They support the hope that systematic studies of the band structure of the transition-series elements can provide useful qualitative, and perhaps quantitative, information concerning their electronic structure.

As in all calculations involving d electrons, the results are sensitive to the choice of potentials. The crystal potentials used in these calculations were all constructed in an analogous manner, and were approximated by a superposition of atomic potentials. The method involves the use of Hartree-Fock solutions to the corresponding atomic problem[3] and the free-electron-exchange approximation.[4] The details of this method for constructing approximate crystal potentials have been described earlier,[5] though a brief resumé is presented in Sec. II of

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[1] J. C. Slater, Phys. Rev. **51**, 846 (1937).
[2] J. H. Wood, Phys. Rev. **126**, 517 (1962).

[3] R. E. Watson, Phys. Rev. **119**, 1934 (1960); R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961).
[4] J. C. Slater, Phys. Rev. **81**, 385 (1951).
[5] L. F. Mattheiss, Phys. Rev. **133**, A1399 (1964).

this paper, along with other information pertaining to this present series of calculations. The energy bands along a single line of symmetry in the appropriate Brillouin zone are presented in Sec. III for Ar, Ti, V, Cr, Fe, Co, Ni, Cu, and Zn, while the last section contains a brief discussion of these results.

II. DESCRIPTION OF THE CALCULATIONS

In these calculations, the crystal potential has been approximated by a superposition of atomic potentials. The Coulomb and exchange contributions to the crystal potential are treated separately. An approximate crystal Coulomb potential and charge density in a given atomic cell is obtained by expanding the neutral atom Coulomb potentials and charge densities of neighboring atoms about the origin, using Löwdin's alpha function expansion,[6] keeping only the $l=0$ or spherically symmetric terms in these expansions. Using the free-electron-exchange approximation, the exchange potenial is proportional to the cube root of the super-imposed atomic-charge densities.

The potentials obtained by this method are generally rather flat near the boundaries of the atomic cell, at least in the case of metals, so they are readily approximated by a "muffin-tin" type potential, as required by the APW method. The constant value of the potential outside the APW spheres is taken as the average value of the potential in this region. This usually results in a discontinuity in the potential at the sphere radius amounting to a few hundredths of a Rydberg.

In the construction of approximate crystal potentials for transition-series elements, there is frequently some ambiguity in choosing the most reasonable atomic configuration. This sort of difficulty can only be answered satisfactorily by experimental information and/or self-consistent energy-band calculations. For the present, we have been content to study the effect that changing the atomic configuration has on the band structure. In addition, there are magnetic effects which create additional complications in this series of elements. For simplicity, all magnetic effects have been neglected in these calculations, and the crystals have been assumed to be nonmagnetic in character.

The lattice constants which have been used in these calculations have generally been the room-temperature values as tabulated by Pearson.[7] The exceptions are those for Ar and Zn. The lattice constant for Ar is the low-temperature value obtained by Dobbs and Jones.[8] In the case of Zn, Harrison[9] has extrapolated the room-temperature lattice constants to low temperatures since the results are expected to be sensitive to the choice of

TABLE I. In this table, we list the elements of the iron transition series, their structures, the lattice constants used in this series of calculations (in atomic units), and the assumed atomic configurations.

Element	Structure	a(au)	c(au)	Configuration
Ar	fcc	10.0346		$(3s)^2(3p)^6$
K				
Ca				
Sc				
Ti	hcp	5.5755	8.8503	$(3d)^3(4s)^1$
V	bcc	5.7225		$(3d)^4(4s)^1$
Cr	bcc	5.4512		$(3d)^5(4s)^1$
Mn				
Fe	bcc	5.4168		$(3d)^7(4s)^1$
Co	fcc	6.6975		$(3d)^8(4s)^1$
Ni	fcc	6.6590		$(3d)^9(4s)^1$
Cu	fcc	6.8309		$(3d)^{10}(4s)^1$
Zn	hcp	5.0120	9.1453	$(3d)^{10}(4s)^2$

c/a ratio. For purposes of comparison, his values have been used in these calculations. Table I contains a summary of the elements considered in these calculations, their structures, the values of the lattice constants, and the assumed atomic configurations.

III. RESULTS

The principal results of these calculations are presented in Fig. 1. These results represent plots of energy as a function of wave vector along lines of symmetry from the center to a boundary of the appropriate Brillouin zones. For the face-centered cubic structure (Ar, Co, Ni, and Cu), the bands are plotted from Γ along the Δ direction to the point X, using the notation of Bouckaert, Smoluchowski, and Wigner.[10] In the body-centered cubic structure (V, Cr, and Fe), the bands are plotted from Γ along the Δ direction to the point H. Finally, in the hexagonal close-packed structure (Ti and Zn), they start at Γ and proceed along the line T in the $k_z=0$ plane which terminates at the point K, one of the vertices of the hexagon (in the notation of Herring[11]).

The energy is in Rydbergs and the wave vectors for the different elements are drawn to scale for purposes of comparison. The horizontal dashed lines represent rough estimates of the Fermi energy for each element. For simplicity, some of the more highly excited bands have been omitted in some cases, particularly in the face-centered cubic structure, or in other situations, they have been sketched in by dashed lines.

In Fig. 2, it is shown what effect varying the atomic configuration has on the band structure of a typical element, namely vanadium. The bands to the right are the ones shown in Fig. 1 for vanadium; the ones to the left are those obtained from a potential which results from an atomic configuration containing an additional $4s$ electron and one less $3d$ electron. In general, this results in a narrowing of the $3d$ band and a decrease in

[6] P. O. Löwdin, Advan. Phys. 5, 1 (1956).

[7] W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys (Pergamon Press, Inc., New York, 1958).

[8] E. R. Dobbs and G. O. Jones, in Reports on Progress in Physics, edited by A. C. Stickland (The Physical Society, London, 1957), Vol. 20, p. 516.

[9] W. A. Harrison, Phys. Rev. 126, 497 (1962).

[10] L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936).
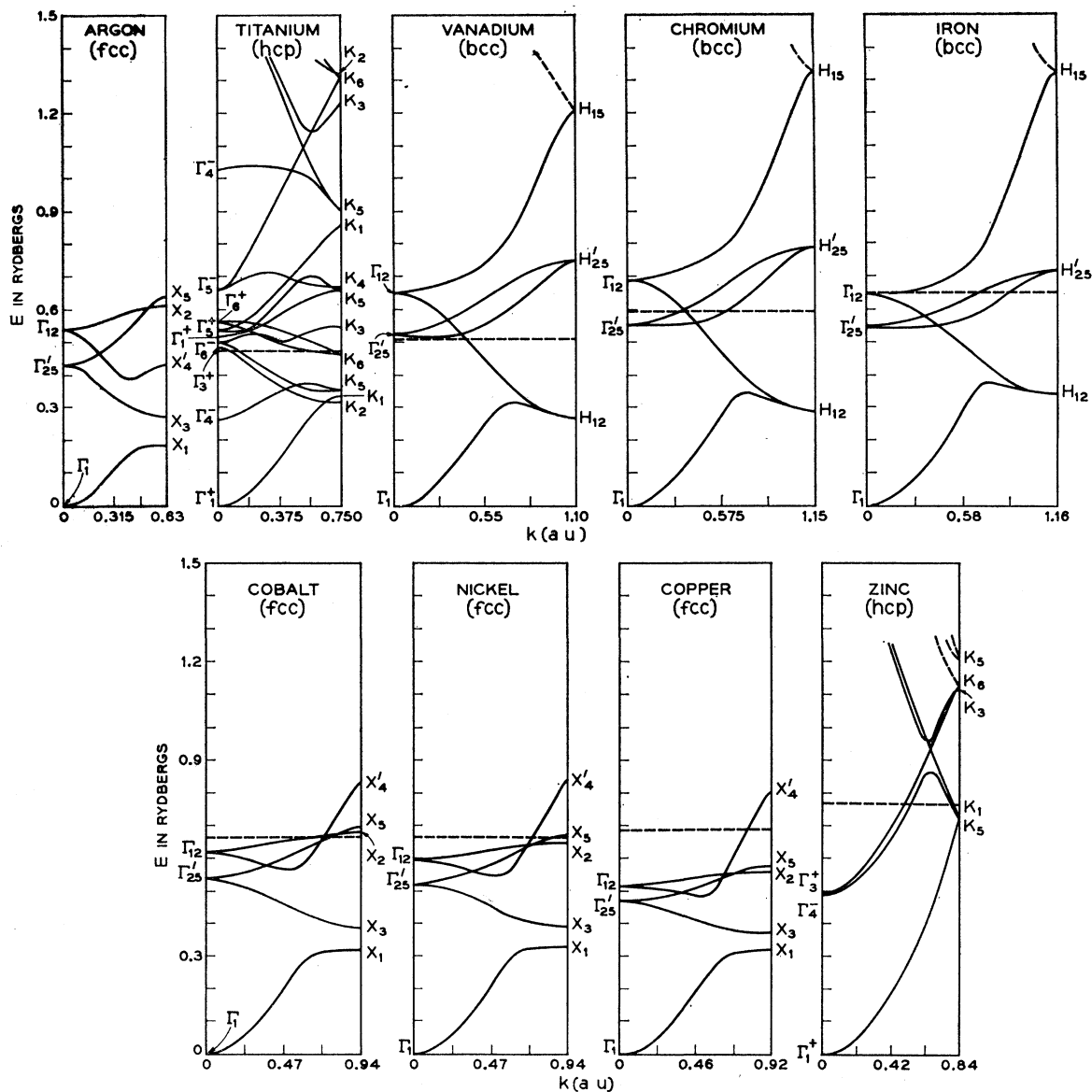
[11] C. Herring, J. Franklin Inst. 233, 525 (1942).

FIG. 1. Energy bands for Ar, Ti, V, Cr, Fe, Co, Ni, Cu, and Zn as a function of wave vector along a line of symmetry in the appropriate Brillouin zone. For the face-centered cubic structure, the bands are plotted from Γ along Δ to the point X. For the body-centered cubic structure, they are plotted from Γ along Δ to the point H. Finally, for the hexagonal close-packed structure, they are plotted from Γ along T to the point K. The energies are in Rydbergs and the wave vectors are in atomic units.

the energy separation between the top of the $3d$ band and the bottom of the $4s$-$4p$ bands.

IV. DISCUSSION

In the simplified picture of the energy bands for the iron transition-series elements, one finds a narrow $3d$ band in the midst of a rather broad $4s$-$4p$ band. The width of the $3d$ band and especially its position relative to the bottom of the $4s$-$4p$ band depend rather critically on the potential. Nevertheless, the results of Fig. 1 exhibit a reasonably smooth variation from element to element, especially for those substances having the

same crystal structure. This seems to lend some support to the rigid band model for the transition-series elements, an approximation which has been of considerable value in understanding the electronic properties of these elements and their alloys.

There is a gradual narrowing of the $3d$ band as one progresses through the series. This effect was discussed by Slater in order to explain the occurrence of ferromagnetism in the latter part of the series.[12] In going from Cu to Zn, the $3d$ band suddenly drops about 0.5 Ry below the bottom of the $4s$-$4p$ bands, and its width

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[12] J. C. Slater, Rev. Mod. Phys. **25**, 199 (1953).

decreases to less than 0.1 Ry. As a result, the energy bands for zinc are very free-electron-like. For those elements where the $3d$ band falls in the middle of the $4s$-$4p$ bands, the interactions between states having the same symmetry causes considerable modification to the free-electron bands, though at points of symmetry, the effect is sometimes small. The bands for Ti and Zn demonstrate this effect nicely.

The results of Fig. 2 emphasize the uncertainty which is inherent in any energy-band calculation for a transition-series element. These uncertainties have been pointed out previously in the literature, particularly by Callaway.[13] These difficulties can only be cleared up satisfactorily with the aid of more detailed experimental information regarding the band structure of these elements in addition to self-consistent energy-band calculations.

The results presented here are not complete enough to permit detailed comparisons to be made with experiment or a discussion of the resulting Fermi surfaces. However, there are some striking similarities between the energy bands shown in Fig. 1 and the results obtained by earlier calculations. In particular, there is good qualitative agreement between the Cu results shown in Fig. 1 and the bands calculated by Segall[14] and also by Burdick.[15] Similarly, the results for Fe are in good agreement with the published results of Wood.[2] The agreement for Ar with the results of calculations by Knox and Bassani[16] is good, and has been described previously.[5] In the case of Cr, it is difficult to compare the present results with those of earlier calculations by Asdente and Friedel[17] since they neglect the interactions between the $3d$ band and the $4s$-$4p$ bands. However, the present results do justify, to some extent, the treatment of Cr by Lomer,[18] who used the results of Wood's iron calculations to discuss the energy bands in antiferromagnetic Cr.

In the case of Zn, the ordering of levels is identical with that obtained by Harrison.[9] This ordering differs from that obtained in earlier calculations for hexagonal
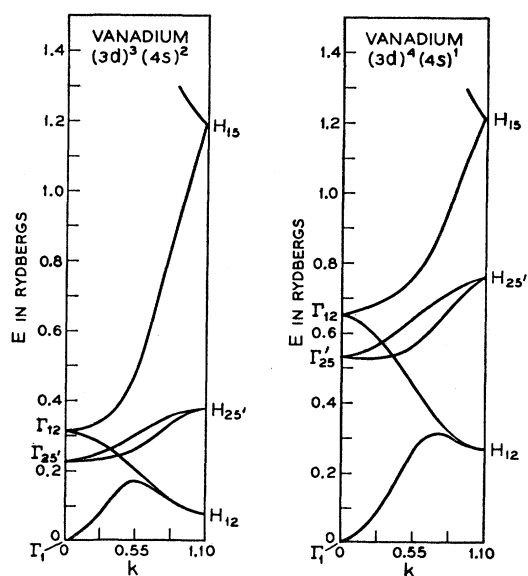

FIG. 2. Energy bands for vanadium along the line Δ obtained from two different potentials. The bands to the left resulted from an atomic configuration of $(3d)^3(4s)^2$ while those to the right involved a $(3d)^4(4s)^1$ configuration.

close-packed metals by Herring and Hill for Be[19] and Falicov for Mg.[20] This change in ordering might be due to the presence of an occupied $3d$ band just below the $4s$-$4p$ bands. The results for Ti agree qualitatively with those obtained by Altmann and Bradley.[21] Finally, the Ni results are in good agreement with those obtained by Hanus.[22]

ACKNOWLEDGMENTS

[13] J. Callaway, Phys. Rev. 99, 500 (1955).
[14] B. Segall, Phys. Rev. 125, 109 (1962).
[15] G. A. Burdick, Phys. Rev. 129, 138 (1963).
[16] R. S. Knox and F. Bassani, Phys. Rev. 124, 652 (1961).
[17] M. Asdente and J. Friedel, Phys. Rev. 124, 384 (1961).
[18] W. M. Lomer, Proc. Phys. Soc. (London) 80, 489 (1962).

[19] C. Herring and A. G. Hill, Phys. Rev. 58, 132 (1940).
[20] L. M. Falicov, Phil. Trans. Roy Soc. A255, 55 (1962).
[21] C. J. Bradley, Ph.D. thesis, Oxford University, 1962 (unpublished).
[22] J. G. Hanus, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Quarterly Progress Report No. 44, p. 29, 1962 (unpublished).