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Electronic structure, superconductivity, and spin fluctuations in the $A15$ compounds A_3B: $A = \mathrm{V}, \mathrm{Nb}$; $B = \mathrm{Ir}, \mathrm{Pt}, \mathrm{Au}$

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The electronic structure of six $A15$ compounds V_3Ir, V_3Pt, V_3Au, Nb_3Ir, Nb_3Pt, and Nb_3Au has been determined by means of self-consistent semirelativistic linear muffin-tin orbital band calculations. Parameters related to superconductivity such as electron-phonon coupling, transition temperature, electronic specific heat, and magnetic exchange enhancement are derived from the electronic-structure results. Generally the results obtained agree well with experimental values, with the exception of Nb_3Pt and V_3Au. In the former compound the density of states (DOS) has a sharp increase at E_F making the exact DOS value uncertain. In V_3Au the high calculated T_c and the Stoner factor indicate that spin fluctuations may be limiting the T_c.

I. INTRODUCTION

In the preceding paper, Ref. 1, we presented various experimental results for A_3B compounds with $A15$ structure; particularly those in which A is vanadium or niobium, and B is iridium, platinum, or gold. These six compounds are not so well studied and famous as the other group with B atoms, such as Si, Ge, Ga, or Sn in which the highest-known superconducting transition temperatures T_c occur, but they are suitable systems for studying influence of V and Nb, since stable well-defined $A15$ structures exist for all the V_3B and Nb_3B combinations. In addition the effect of the B element is strong so that the Ir compounds have low T_c's and electronic specific heat coefficients γ, whereas the Au compounds have relatively high T_c's and γ's. In this paper we present theoretical results for the electronic structure in the six compounds, and derive various physical properties. Use of phonon moments determined in Ref. 1 allows us to calculate the electron-phonon coupling parameters λ from the electronic structure, which subsequently are used to get theoretically determined values of T_c and γ. Special attention has been paid to the possible role of spin fluctuations and its T_c limiting effects, and magnetic exchange enhancement factors have been derived but otherwise we have not attempted to use available theories[2] for directly calculating the spin-fluctuation contributions to λ. These theories ought to be tested first on less complicated systems.

Here we have used the linear muffin-tin orbital (LMTO) band method[3,4] for the electronic-structure calculations, which have been applied earlier to $A15$ compounds.[4,5] We have improved the accuracy of the results mainly by improving the k-point sampling. Of the group of compounds presented here only V_3Au was studied in the earlier calculations[5]; otherwise this is to our knowledge the first electronic-structure calculation done for $A15$ compounds of this composition.

The $A15$ structure is by now very well known. The unit cell consists of two formula units. The B atoms occupy bcc-type positions in the simple cubic unit cell whereas the A atoms sit in pairs on the cube surfaces, which contribute to three sets of "linear chains" each parallel to one cube axis. Nonstoichiometry and lattice instabilities are common among the $A15$'s but not so much in the systems studied here; the calculations assume a perfect unit cell. We used the experimental lattice constants given in Ref. 1.

In Sec. II some details of the electronic-structure calculation are given. Section III describes the calculations of the various physical parameters, the results obtained, and discusses the results and approximations involved.

II. DETAILS OF THE CALCULATIONS

As in our earlier calculations we determined the electronic structure for each compound with the use of the self-consistent semirelativistic linear muffin-tin orbital band method (LMTO).[3–6] This method uses spherically symmetric potentials in overlapping muffin-tin (MT) spheres with the "combined correction" terms[3] included to correct eigenvalues for the overlapping geometry and to improve l convergence.

The basis set included *s,p,d* for all atoms and *s,p,d,f* in the three-center terms.[4] The wave vectors $A_{j,L}^{\vec{k}}$ are constructed so as to account for tail contributions[4] and the final wave function has the form

$$\psi_L^{\vec{k}}(r)=A_{j,L}^{\vec{k}}R_{ql}(E_j r)Y_L(\hat{r}) - \sum_{L'}\tilde{R}_{l'}(E_j r)A_{jL'}^{\vec{k}}S_{LL'}^{\vec{k}} , \qquad (1)$$

where R_{ql} is radial wave function for atom q and angular momentum l ($L=q,l,m$) and $S_{LL'}^{\vec{k}}$ is the structure matrix. By allowing the wave function to include f ($l=3$) from the second term in Eq. (1), it is to a good approximation possible to take the f character in the wave function into account without having to include it in the direct terms of basis functions. Thus the eigenvalue problem is of rank 72 instead of 128 as it would be otherwise. In a calculation on V_3Si a reduced basis set using no direct d basis for the Si sites, was tried in order to reduce the eigenvalue problem from rank 72 to 62. The main features of the band structure were similar as for the normal basis; however, on a fine energy scale essential differences could be seen. In particular, the high peak in the density of states (DOS) coming from the very flat Γ_{12} state was about 4 mRy below E_F using the reduced basis, while 2 mRy above E_F otherwise. Mattheiss and Weber,[7] with the use of a tight-binding fit to augmented plane wave (APW) results also obtained the Γ_{12} state about 2 mRy above E_F which is important to explain the tetragonal distortion in V_3Si. We have therefore used the normal basis set in all calculations (i.e., with d also for the B site), even though the d DOS for Si or Au is very low at E_F. Moreover the Fermi surface obtained for V_3Si agrees very well (to within 3 mRy) with results obtained from positron annihilation experiments.[8] Thus a similar degree of accuracy is expected also for the compounds studied here as long as no relativistic spin-orbit coupling corrections become important. The radial valence functions were determined using a semirelativistic solution of the Dirac equation[9] and the core functions are fully relativistic and recalculated in each iteration. This is in contrast to the earlier *A* 15 calculations[4] where the core functions were frozen. The self-consistency procedure is made efficient by using a canonical band scheme[4] in the initial stage of the iterating process. The Madelung contribution to the potential was determined in a nonoverlapping-sphere geometry[4] in which the itinerant and localized charge distributions are treated differently. The overlapping Wigner-Seitz (WS) spheres, which were chosen to have identical radii in the earlier *A*15 calculations, are now $0.320a$ for B sites and $0.307a$ for A sites, where a is the lattice constant. The self-consistent convergence is less than ±2 mRy for states below E_F which is somewhat better than for the earlier *A*15 calculations.[4]

All mentioned improvements and differences in the calculations with respect to the earlier *A*15 LMTO calculations are probably of minor importance. However, here we have in the final iteration used 120 k points in the irreducible Brillouin zone (IBZ) compared to 35 or 20 earlier. Moreover, we now also use tetrahedron integration[10] and/or 27-point quadratic interpolation to improve the DOS determination. This allows us to give DOS values at E_F within 3 mRy resolution compared to 10 earlier.[4,11] On the other hand we have not yet tried to include the effects of band crossing on the DOS determination, but such effects are probably small.

The quadratic interpolation method works as follows: Around each k point, the bands are interpolated quadratically in k_x, k_y, and k_z using the 27 nearest k points, reflected in the zone boundaries if necessary, to create an analytical description of the bands in the inscribed volume. (Trying to use only 7 points to interpolate independently along the k_x, k_y, and k_z directions occasionally gave poor bands along the [111] direction.) The bands are then locally described by a function $\epsilon(k_x,k_y,k_z)$ from which an arbitrarily fine k mesh can be generated. For finding the x, y, and z components of the band velocities it is easy to analytically take the k_x,k_y, or k_z derivatives of ϵ and generate their values in the same mesh.

III. RESULTS

In the corresponding Figs. 1(a)—6(a) the band structure is shown and in Figs. 1(b)—6(b) the density of states versus energy is given for all compounds. The DOS figures are obtained directly from the 120 k points by use of tetrahedron k-point integration method.[10] One can see in V_3Pt and Nb_3Pt that the Fermi energy falls on a sharp rise in the DOS versus energy curve, making the exact value for $N(E_F)$ somewhat uncertain. In another calculation the 120 points were used to interpolate into a finer mesh of 2024 points in the irreducible Brillouin zone (IBZ) from which another value of $N(E_F)$ was obtained. The two methods give very similar values. In Table I we give their average. The widths of the energy bins of the histograms used to construct the DOS was 2 mRy. The error limits shown are defined from the DOS values in the adjacent energy bins. As seen for V_3Pt and Nb_3Pt the DOS values are uncertain to about 20%, while for the other compounds the DOS values are more certain. From Table I it is also seen that the V- or Nb-d contributions always dominate the bands around E_F. The

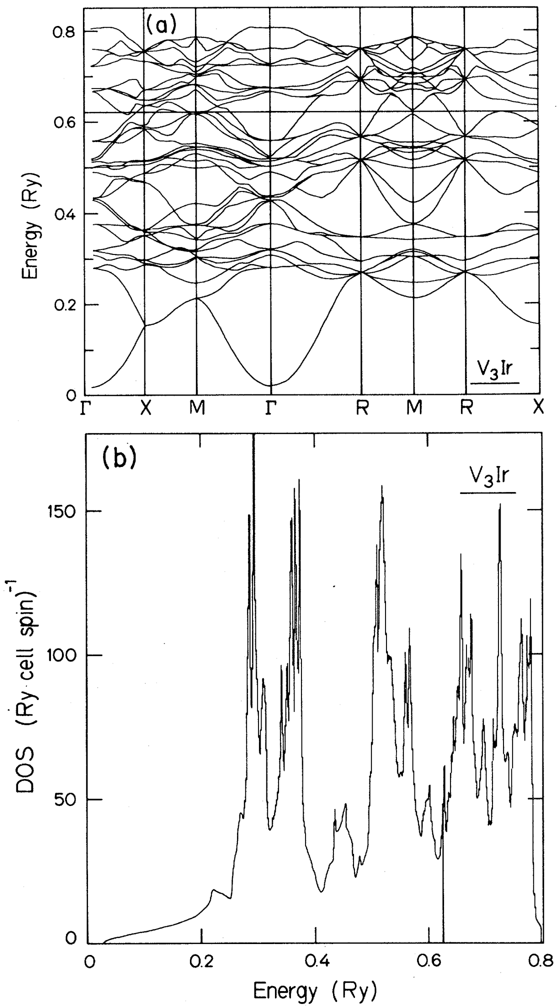

FIG. 1. (a) Band structure along symmetry directions obtained from 120 k points in the IBZ for V_3Ir. (b) Total density of states (DOS) obtained using tetrahedron k-point integration for V_3Ir.

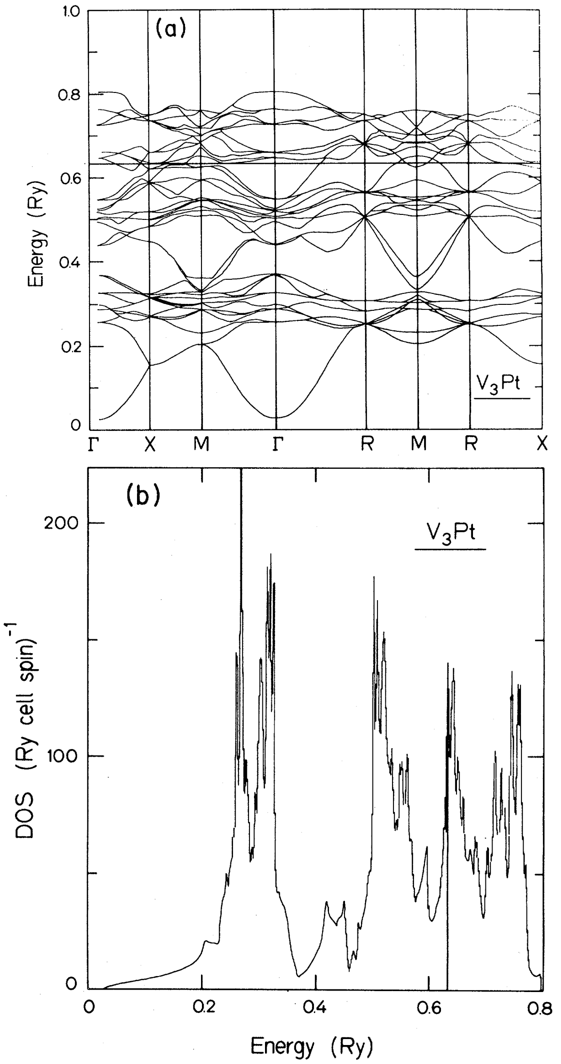

FIG. 2. (a) Band structure along symmetry directions obtained from 120 k points in the IBZ for V_3Pt. (b) Total density of states (DOS) obtained using tetrahedron k-point integration for V_3Pt.

B-atom d-band contributions are very small, except in Nb_3Ir where it is 20% of the total, so that the effects of neglecting the spin-orbit coupling are probably minor for properties which are dependent on the $N(E_F)$. Going from the Ir to Au compounds one sees from the figures how the B atom d bands separate out due to increased localization of the wave function. Here the effect of spin-orbit coupling is of course important. For comparison with x-ray photoemission spectroscopy (XPS) spectra, for example, an additional splitting of about 1 eV has to be included for the Au d band.[4]

The function of the B atoms in our compounds is to stabilize the structure and to determine the Fermi energy. On the other hand, it seems from our preceding remarks on band separation and localization that the B atoms are not directly involved in the superconductivity. The local d DOS on the B site is low at E_F despite the fact that at least fcc Pt and Ir have large amounts of d electrons at E_F.

Looking at the charge content within spheres within radii nearly equal to nonoverlapping muffin tins, and within the remaining interstitial region (see Table II) one notes a localization of the B-site charge when going from the Ir- to the Au-compound result. The charge difference within B spheres between Ir and Pt, and between Pt and Au is larger than one unit and charge is pulled away from the interstitial region, whereas the charge on V or Nb remains nearly constant. Somewhat unexpected-

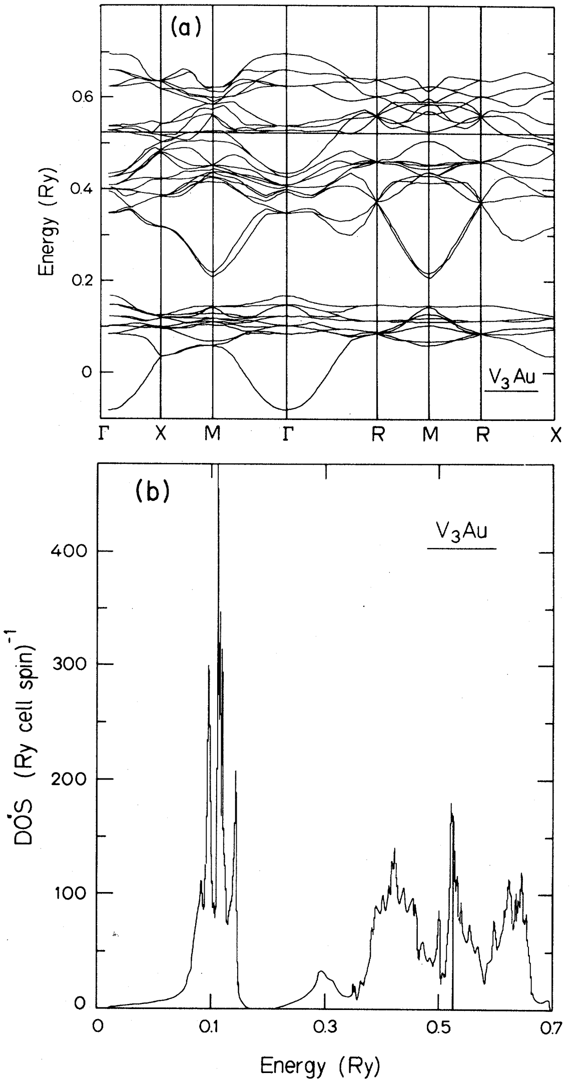

FIG. 3. (a) Band structure along symmetry directions obtained from 120 k points in the IBZ for V_3Au. (b) Total density of states (DOS) obtained using tetrahedron k-point integration for V_3Au.

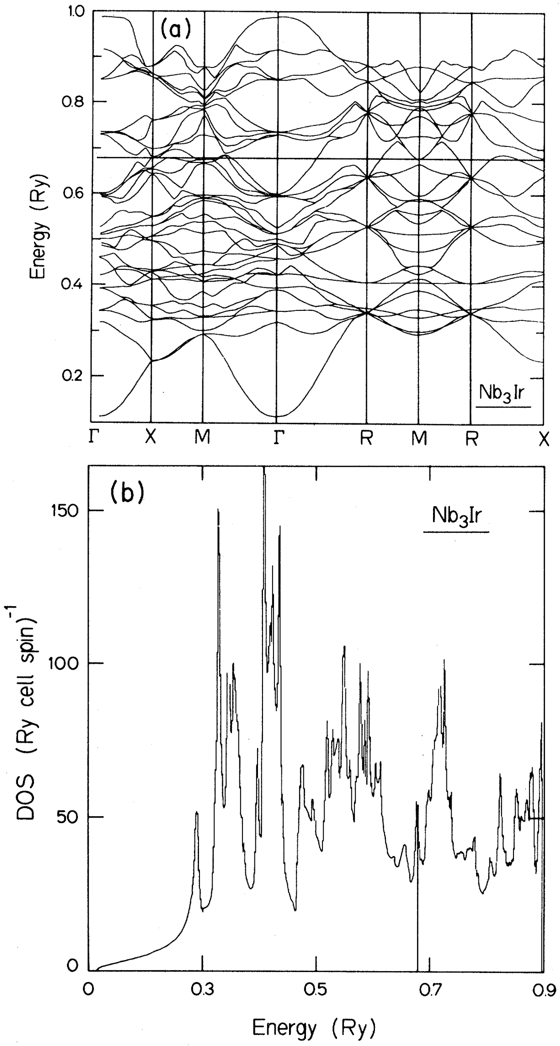

FIG. 4. (a) Band structure along symmetry directions obtained from 120 k points in the IBZ for Nb_3Ir. (b) Total density of states (DOS) obtained using tetrahedron k-point integration for Nb_3Ir.

TABLE I. Density of state values, total and partial, per rydberg, unit cell, and spin at the Fermi energy for each compound. Nb_3Pt II is with E_F moved 4 mRy upwards. The errorbars indicated for the total DOS, are obtained from DOS values within 2 mRy from the correct Fermi energy. See the text for details about the DOS determination.

	A				*B*				
	s	*p*	*d*	*f*	*s*	*p*	*d*	*f*	Total
V_3Ir	0.8	3.4	26	0.4	0.5	1.3	5.4	0.0	38 ± 1
V_3Pt	0.7	5.4	72	1.0	1.1	2.1	11	0.1	93^{+20}_{-10}
V_3Au	1.7	10.7	133	1.8	1.2	3.4	9.0	0.2	161 ± 10
Nb_3Ir	1.2	3.7	29	0.8	1.1	1.8	9.3	0.1	47 ± 4
Nb_3Pt I	0.5	3.0	44	0.9	2.0	2.5	13	0.1	67^{+15}_{-10}
II	0.8	4.9	62	1.3	2.5	3.4	15	0.3	90 ± 15
Nb_3Au	1.6	8.2	93	1.8	2.7	4.4	7.5	0.4	120 ± 5

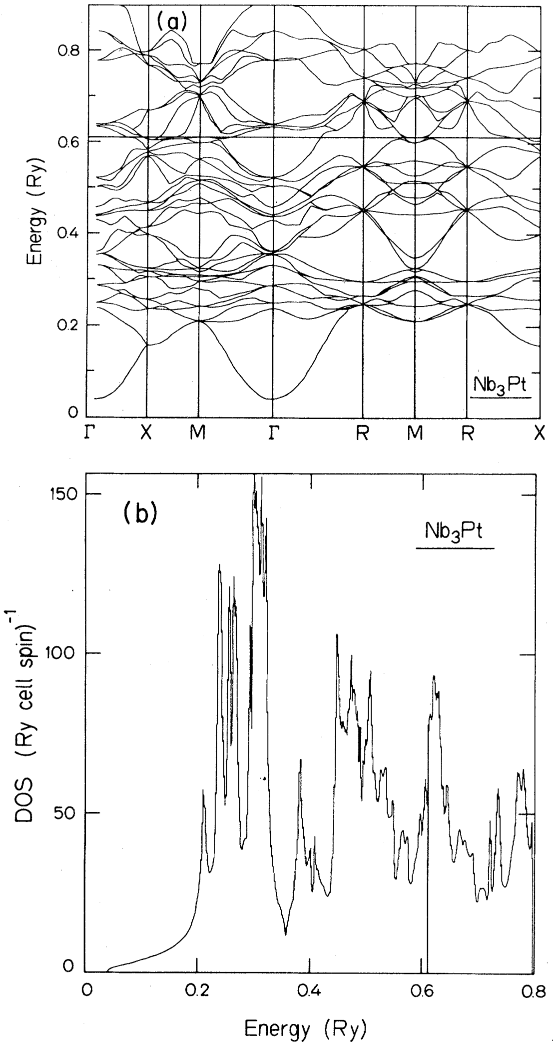

FIG. 5. (a) Band structure along symmetry directions obtained from 120 k points in the IBZ for Nb$_3$Pt. (b) Total density of states (DOS) obtained using tetrahedron k-point integration for Nb$_3$Pt.

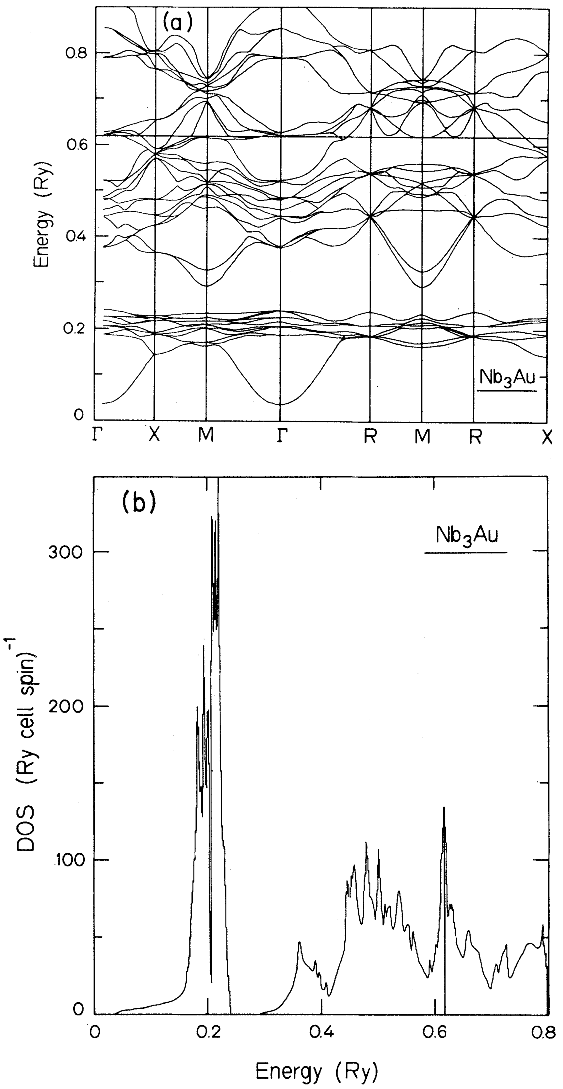

FIG. 6. (a) Band structure along symmetry directions obtained from 120 k points in the IBZ for Nb$_3$Au. (b) Total density of states (DOS) obtained using tetrahedron k-point integration for Nb$_3$Au.

TABLE II. Number of electrons per A and B MT sphere and interstitial charge, calculated pressures using overlapping spheres and obtained band velocities at E_F. The MT spheres are approximately the same as the touching nonoverlapping spheres so that $R^A_{\mathrm{MT}}=0.253a$, $R^B_{\mathrm{MT}}=0.296a$, and interstitial volume is then $0.375a^3$ where a is the lattice constant taken from Ref. 1.

	Valence charge distribution (electrons)			Pressure (kbar)			
	A	B	Interstitial	A	B	Total	$\langle v_F \rangle [10^5\ m/s]$
V$_3$Ir	3.48	8.31	10.52	−160	420	−1	2.69±0.05
V$_3$Pt	3.47	9.50	10.20	−240	500	−35	1.16±0.03
V$_3$Au	3.48	10.65	9.80	−310	620	−53	1.08±0.03
Nb$_3$Ir	2.99	9.19	11.66	−100	660	104	3.01±0.15
Nb$_3$Pt	3.00	10.31	11.40	−140	740	99	1.57±0.05
Nb$_3$Au	3.01	11.47	11.02	−210	877	88	1.84±0.03

ly, one finds no charge transfer to the *A* sites when the *B* sites give additional electrons to the structure but the Fermi energy moves upward filling the *A-d* band. This can be interpreted as a delocalization of the *A-d* electrons of high energy. The interstitial charge is not increasing, but the *B*-site localization attracts the interstitial electrons to a larger extent. This rather complex behavior of the charge rearrangement during the increased occupation of the *A-d* band indicates that a rigid-band model of the *A-d* band would not apply to these systems. Also from Figs. 1–6 it is seen that in detail the band structures differ substantially from compound to compound.

Taking the lattice constants into account and using the interstitial charge values one finds that the interstitial charge densities decrease going from V to Nb and from Ir to Au. This correlates with the phonon frequencies so that low charge density gives low Debye temperature. The same trend was also found for the type of *A*15 compounds with nontransition elements on the *B* site.[4] Finally, one can observe from the charge values that the V atoms are relatively more localized than the Nb atoms. This is due to the different behavior of the 3*d* and 4*d* electrons and affects the lattice stiffness and electron-phonon coupling properties. The atom on the *B* site is less localized in the V compound than in the Nb compound.

The electron-phonon coupling λ has been calculated from the LMTO results using isotropic wave functions and constant phonon frequencies separated from the electronic part. Thus λ is separated into an electronic numerator and the phononic denominator[12] and using LMTO parameters we have

$$\lambda=\frac{\eta}{M\langle\omega^2\rangle}\;, \tag{2}$$

where

$$\eta=\frac{1}{N}\sum_l \frac{(l+1)N_lN_{l+1}(P_{l+1}-P_l)^2R_l^2R_{l+1}^2}{2(2l+1)(2l+3)(j_lP_l-n_l)^2(j_{l+1}P_{l+1}-n_{l+1})^2} \tag{3}$$

$$P_l=(2l+1)\frac{D_l+l+1}{D_l-1}\;. \tag{4}$$

D_l is the logarithmic derivative, R_l is the radial part of the wave function, and j_l and n_l, the amplitude of the wave-function Bessel and Neumann functions. R_l, j_l, and n_l are evaluated at the WS radius. M is atomic mass. $(\langle\omega^2\rangle)^{1/2}$ the averaged phonon frequency taken from the measured data by Junod *et al.*[1] is defined as

$$\langle\omega^2\rangle=\frac{\int \alpha^2F(\omega)\omega\,d\omega}{\int \alpha^2F(\omega)d\omega/\omega}\;, \tag{5}$$

with the assumption that $\alpha^2\sim\omega^{-1/2}$.

Unfortunately, the measurements give no information about the partial character of the phonon spectrum. This would be very valuable information since one then could separate λ into *A* and *B* atom contributions,

$$\lambda=\frac{\eta_A}{M_A\langle\omega_A^2\rangle}+\frac{\eta_B}{M_B\langle\omega_B^2\rangle}\;. \tag{6}$$

As was implied from the local DOS data, and confirmed from calculated η values, η_A is much larger than η_B by almost two orders of magnitude. Thus it is of importance to know the local $\langle\omega_A^2\rangle$ rather than the total $\langle\omega_{A_3B}^2\rangle$ moments, since they couple directly with the η_A electronic part. To get a local $\langle\omega^2\rangle$ decomposition we have assumed that they scale with the Debye temperatures Θ of this pure *A* and *B* materials. Thus $\langle\omega_A^2\rangle$ and $\langle\omega_B^2\rangle$ values are determined from the measured $\langle\omega_{A_3B}^2\rangle$ and Θ_A,Θ_B values from the following equations:

$$\begin{aligned}(N_A+N_B)\langle\omega_{A_3B}^2\rangle^{1/2}&=N_A\langle\omega_A^2\rangle^{1/2}\\&\quad+N_B\langle\omega_B^2\rangle^{1/2}\;,\\ \Theta_B\langle\omega_A^2\rangle^{1/2}&=\Theta_A\langle\omega_B^2\rangle^{1/2}\;,\end{aligned} \tag{7}$$

where N_A and N_B are the number of *A* and *B* atoms, respectively. The results of this decomposition are shown in Table III; somewhat surprisingly it is found that the local values of $\langle\omega^2\rangle^{1/2}$ for any element always are the same to within 2 K, independent of which compound it is part of. This implies two things: First, the measured $\langle\omega_{A_3B}^2\rangle$ values are probably accurately and consistently derived. Second, the six compounds have all similar phonon spectra; no unique phonon softening takes place in any of the compounds since then the measured $\langle\omega_{A_3B}^2\rangle$ value would not fit within the model with constant $\langle\omega_A^2\rangle$ and $\langle\omega_B^2\rangle$ values. It would be interesting to do a similar analysis for the other types of *A* 15's with *B* atoms like Al, Ga, Ge, Si, and Sn, where, for instance, Nb_3Sn is believed to exhibit phonon softening related to the superconductivity. However, here precise phonon data are missing part-ly due to material problems. Since not all of these B elements form stable $A15$ structures with both V and Nb, no complete comparison can be made.

As seen from Table III, the use of local $\langle\omega^2\rangle$ values rather than the measured $\langle\omega^2_{A_3B}\rangle$ directly, tends to decrease the calculated λ values, in particular for the V_3Au and Nb_3Au compounds. This is of course a result of the soft, low-frequency Au Θ_D values compared to those for V and Nb.

In the calculation of η the l summation goes from 0 to 2. Thus it is important to have the accurate partial f DOS to get the proper d-f scattering contribution. The procedure to approximate the f character by use of Eq. (1) is convenient and accurate.[4] In the earlier LMTO values for λ in $A15$ compounds[4] the f DOS was assumed to be equal to the DOS of the "free scatterer." However, the tail f DOS used here is more accurate, comparable to the one obtained by using the full f basis.

The resulting λ values are shown in Table IV together with the decomposition from the different sites. It is evident that the V and Nb atoms make the main contribution. This is the situation also for $A15$'s with Si, Ge, etc., on the B sites. On the other hand, with Ir or Pt on the B site, one might have expected a substantial contribution to λ since the pure elements have a high DOS. The theoretical value obtained for Nb_3Pt is unexpectedly low since its T_c is over 10 K. However, here the E_F falls just on the low side of a sharp rise in the (Nb-d) DOS. In another value for Nb_3Pt, labeled II, the Fermi energy has been increased 4 mRy, which corresponds to 50.5 electrons per unit cell instead of 50.0. The DOS value has now increased about 50% as well as λ, which now is more realistically 0.90. This extreme sensitivity for Nb_3Pt, due to the rapid variation of the DOS around E_F, makes small inaccuracies in the band calculation very prominent. The exact cause for the slightly too-low Fermi energy in Nb_3Pt is difficult to point out. However, errors at the order at 4 mRy at this energy could be due to the neglect of spin-orbit coupling and nonspherical corrections to the potential. Another cause could be that the exact Fermi energy would be misplaced because a band crossing at E_F could have been missed in the DOS determinations. As can be seen in Fig. 4 such a case occurs in Nb_3Ir along the M-Γ line. In V_3Pt the DOS has a rapid variation near E_F. As seen earlier in the case of Nb_3Pt this can lead to errors, but our value for λ in V_3Pt is reasonable, and therefore we did not try to change E_F. The compounds with Ir and Au do not show the same sensitivity because their DOS does not vary rapidly near E_F.

TABLE III. Measured phonon moments (in K) for the different compounds $\langle\omega_{A_3B}\rangle^{1/2}$ and $\omega_{\log}$ of Ref. 1 and the component derived $\langle\omega_A^2\rangle$ and $\langle\omega_B^2\rangle$ using Eq. (7). The Debye temperatures used in this derivation are taken from C. Kittel, *Introduction to Solid State Physics*, 4th ed. (Wiley, New York, 1971), and are V:380, Nb:275, Ir:420, Pt:240, and Au:165 K.

A_3B	$\langle\omega^2_{A_3B}\rangle^{1/2}$	$\langle\omega^2_A\rangle^{1/2}$	$\langle\omega^2_B\rangle^{1/2}$	$\omega_{\log}$
V_3Ir	254	247	273	204
V_3Pt	225	248	156	180
V_3Au	211	246	107	154
Nb_3Ir	203	179	274	172
Nb_3Pt	175	180	158	141
Nb_3Au	164	182	109	122

The electronic specific heat coefficient γ can now be derived from the calculated DOS and λ values using the formula

$$\gamma=\frac{2\pi^2}{3}k_B^2N(E_F)(1+\lambda)\ . \tag{8}$$

The results are shown in Table IV together with measured values.[1] (Note the calculation has not included effects from spin fluctuations.) As seen the agreement between calculated and experimental values is quite good except for V_3Au where the calculated γ is about 25% too high and also for Nb_3Au where the deviation is about 30%. In V_3Au it was found experimentally[1] that extended heat treatment during several weeks or months, steadily increases γ. It is difficult to estimate at which value γ finally saturates for "perfect" $A15$ V_3Au, but the mentioned discrepancies between calculated and measured γ values will be reduced to some extent but not completely. This is an indication that the calculated DOS or λ are somewhat too high for the high DOS compounds V_3Au and Nb_3Au.

Next, in Table IV we show the calculated superconducting transition temperatures T_c, obtained from the calculated λ values, the measured values for $\omega_{\log}$ (Ref. 1) and the parametrized values for μ^*. The μ^* was calculated using[13]

$$\mu^*=\frac{0.26N}{1+N}\ , \tag{9}$$

where N is the DOS per eV atom (otherwise in this paper N is per Ry, cell, and spin) and T_c is given by the McMillan formula[14]

$$T_c=\frac{\omega_{\log}}{1.2}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right]\ . \tag{10}$$

For our values of N, μ^* falls within the range between 0.12 and 0.20 when going from the low to the high DOS materials. To calculate the T_c's is a more difficult task than the γ's. A complete calculation requires information about the phonon spectra. We have used the McMillan expression; therefore the values obtained must be viewed as very approximate. In general the Nb compounds give too-low values. The low T_c compounds with Ir on the B sites are less interesting because it is doubtful that a strong coupling formula such as Eq. (10) is applicable. For the compounds containing Pt, there is as mentioned before, additional uncertainties of the exact DOS value at E_F. In V_3Pt the obtained T_c is of the correct magnitude, as well as its γ value. For V_3Ir, V_3Pt, Nb_3Ir, and Nb_3Au, the T_c results can be considered as being within realistically defined "errorbars" for this type of calculations. Surprisingly the T_c value for Nb_3Pt is too low by almost 1 order of magnitude. Not even the result indicated Nb_3Pt II, obtained from a rigid-band shift of the E_F at 4 mRy, gives a correct T_c. It is still only 55% of the measured value.

It is interesting to compare the results for the two compounds containing Au. As seen Nb_3Au gives a nearly correct T_c (~ 9 K), whereas in V_3Au 10 K is obtained, which is almost 1 order of magnitude too high and is outside the generously defined errorbars. This implies that some other mechanism, such as spin fluctuations, is present in V_3Au and limits its otherwise very high T_c. On the other hand, from the quite good calculated T_c for Nb_3Au, with the use of the approximate theory which does not include spin fluctuations in Nb_3Au, one may preclude strong effects of spin fluctuations in Nb_3Au.

The calculated T_c's in V_3Pt is nearly correct but in V_3Au the experimental value is much lower. Experimentally there is practically no difference between the two compounds.

In the previous paper, Ref. 1, the McMillan equation (10) was inverted to obtain an experimental λ from the measured T_c. These values differ sometimes significantly from the calculated λ's shown in Table IV; for instance, for V_3Au by a factor of 2. Using these "experimental" λ values together with the measured specific heat, Eq. (8), an experimental DOS value is derived. By this procedure one obtains fairly good agreement with the calculated-band DOS values, usually around 20% even for V_3Au and Nb_3Pt. However, this agreement is not always realistic concerning the λ, which connects the γ and T_c. For example, in the case of V_3Au it would be difficult to understand why from the measured T_c and γ, one obtains a very high DOS (1.72 states per eV atom) together with a very low λ (0.62). In reality λ is probably higher (and DOS lower), but T_c is lowered by spin fluctuations, whose influence we did not include.

To proceed to investigate the possibilities for spin fluctuations in these systems we calculated the Stoner factors which tell how close to the ferromagnetic regime a compound is. Usually one writes the Stoner factor S as exchange enhancement of the magnetic susceptibility χ:

$$\frac{\chi}{\chi_0} = S = \frac{1}{1-NI} = \frac{1}{1-\bar{S}} , \qquad (11)$$

where N is the DOS and I is an exchange-correlation integral. For multiband compounds there is a combination of several contributions, but without going into detail it is possible to derive a corresponding number of $\bar{S}$ also for a compound.[15] In the case of compounds the $\bar{S}$ values are quadratically dependent on the local DOS and thus it is clear that the V and Nb atoms gives the dominant contributions to $\bar{S}$, about 98%. In Table IV the calculated $\bar{S}$ values are shown with the use of the Gunnarson-Lundqvist local-spin-density (LSD) functional[16] in the evaluation of the exchange-correlation integrals. In V_3Au $\bar{S}$ is 1.2 which is beyond the limit for ferromagnetism and therefore too high. Also for the other materials it seems that the calculated $\bar{S}$ values are somewhat too high. Using another LSD functional might give as overall reduction of $\sim 5\%$ through the I integrals. But still 10–15 % has to be accounted for in V_3Au to bring $\bar{S}$ below one. The results indicate furthermore that the calculated DOS value, N, is also too high, of the order of 10% or more in

TABLE IV. Calculated λ values, its site decomposition, specific heat γ, superconducting transition temperature T_c, and Stoner parameter $\bar{S}$ for each compound. Experimental γ and T_c values of Ref. 1 are given as comparison.

	λ			γ(mJ/g-at. K^2)		T_c (K)		$\bar{S}$
	A	B	Total	Calc.	Expt.	Calc.	Expt.	
V_3Ir	0.30	0.01	0.31	2.1	1.9	0.1	<0.015	0.25
V_3Pt	0.64	0.04	0.68	6.8	7.1	3.0	2.7	0.64
V_3Au	1.23	0.06	1.30	16.6	13.1	10.2	2.8	1.2
Nb_3Ir	0.50	0.02	0.52	3.1	2.0	1.8	1.5	0.23
Nb_3Pt I	0.53	0.06	0.60	4.7	6.2	1.8	10.0	0.43
II	0.80	0.09	0.90	7.4		5.5		0.51
Nb_3Au	1.18	0.09	1.27	11.8	9.0	8.5	10.6	0.74

V_3Au. In the other compounds it is more difficult to say.

The enhancement factors obtained from experiment[1] allow one to determine $\bar{S}$ values for Nb_3Au, Nb_3Pt, and V_3Au. The value for Nb_3Pt agrees quite well with the calculated Nb_3Pt (II) value, but here other properties indicated that the DOS was too low. For Nb_3Au the calculated value is about 30% too high and in V_3Au, 60%. Similar calculations[17] of Stoner factors in pure elements usually work satisfactorily, within 10–15%. By self-consistent spin-polarized band calculations including an applied field,[18] a more accurate determination of S and $\bar{S}$ is possible but then the computational effort increases drastically.

In consideration of the difficulties in obtaining realistic and exact $\bar{S}$ values, we have not attempted to use the approximate prescriptions of deriving spin-fluctuation contributions to λ (λ-spin) from the $\bar{S}$ values. Instead we want to use the $\bar{S}$ values for a qualitative internal comparison among the compounds.

Obviously, V_3Au with the highest $\bar{S}$ is likely to have spin fluctuations. Experimentally, with prolonged heat treatment the susceptibility is steadily increasing[1] indicating that V_3Au is not far from the ferromagnetic transition, probably more enhanced than any other $A15$ compound. This compound, V_3Au, with its still observable T_c of 2.8 K, might be a good system for studying spin fluctuations, especially if with magnetic impurities or some other treatment, the susceptibility can be enhanced further until its T_c is suppressed. Of the other compounds V_3Pt and Nb_3Au have quite large $\bar{S}$ values, 0.64 and 0.74, respectively. Whether it is enough to reduce T_c is an open question. However, for comparison these $\bar{S}$ values are larger than obtained for pure V or Nb.

In Table II the Fermi velocities $\langle v_F \rangle$ are given as obtained from the quadratic interpolation. A direct comparison with experiment is difficult to make, but one might try a comparison with H^*_{c2}, the orbital upper critical field[19] which is inversely proportional to $\langle v_F^2 \rangle$:

$$H^*_{c2} = \frac{2\pi^2 k_B^2 T_c}{e\hbar} \frac{(1+\lambda)^2}{v_F^2} . \tag{12}$$

For Nb_3Au the calculated H^*_{c2} is only about 15% of the experimental value, whereas for the other calculated properties Nb_3Au is a system which gave good agreement with experiments. This stresses the fact that it is particularly difficult to calculate H^*_{c2} from calculated properties only. Of the compounds for which comparison with experiment is possible, the calculated values are far too low, except for V_3Au where it is too large. This latter exception might be due to spin fluctuations.

The results obtained from the band calculations have clearly shown the trends and differences for the six compounds and the physically interesting properties have been revealed. But, as has been mentioned, Nb_3Pt has its problems due to the sharp rise in the DOS at E_F and various indications have implied that the obtained DOS at E_F in V_3Au and perhaps also Nb_3Au is somewhat too high. Possible causes of the difficulties in Nb_3Pt have been discussed earlier; neglect of spin-orbit coupling and band crossing around E_F may have led to a displacement of the Fermi energy. Also the effects of neglecting nonspherical contributions to the potential are possible, and this may cause a band-narrowing effect to explain the too-high DOS in V_3Au. Namely, the V atoms form the "linear-chain" structure in the $A15$ compounds and a nonspherical V potential would be likely to open up a "channel" for increased d-d interaction along the chain directions. In general increased interatomic interaction results in a band widening which leads to lower DOS values.

The calculated pressures shown in Table II indicate a possible insufficient interatomic interaction especially for the V compounds. The total pressures being negative for V_3Pt and V_3Au hint that the lattice parameters used in the calculation were slightly too large to give stable interatomic interactions. Next, by looking at the partial site decomposed pressure results we see that the V and Nb sites always have negative pressures, i.e., insufficient interatomic interaction. The Nb and especially the V atoms are in the calculations too isolated and this may of course show up as too-narrow d bands. Pressures of the order of 100 kbar are very large on an experimental scale, but they correspond only to about 1% in the lattice constant for not-too-soft materials. It is possible that using slightly smaller lattice constants than the experimental ones used in these calculations, would describe the d bands more in agreement with the true situation. However, other parts of the band structure would be affected and the best approach would of course be to include the nonspherical effects self-consistently.

Next one can ask if one can get values for the DOS which is too high while at the same time obtaining a good Fermi surface (FS). As was mentioned earlier positron experiments[8] indicated that the calculated FS was good to within 3 mRy for V_3Si, while de Haas–van Alphen (dHvA) measurements[20] in the low DOS $A15$ compound Nb_3Sb claimed that the earlier LMTO calculation was mainly correct apart from a 30 mRy deviation at the M point. Obviously a uniform scaling of a given band structure does not change the FS at all, while it changes the Fermi velocity or band mass.

Relative shifts of different bands change in principle the FS topology and may be caused by nonspherical potential corrections. The important factor is how the symmetry of a given state projects on the symmetry of the potential correction and the amplitude of the shift scales with the amplitude of the correction term. The very good result for V_3Si may be due to the high DOS of a flat band which "pins" the Fermi energy to it, whereas in a low DOS material the Fermi energy does not follow a certain band to the same extent. Thus a correct FS topology is possible in V_3Si and V_3Au even with too-high DOS at E_F.

IV. CONCLUSION

The electronic structure has been calculated for six *A*15 compounds and physical properties related to superconductivity have been extracted from it. The complete set of experimental data for all these compounds has made systematic comparison between calculation and measurements possible. There is in general a good agreement and for most properties in these *A*15 compounds, the behavior is understood within the existing theories for superconductivity. The results for Nb_3Pt is less good, since the DOS at E_F increases rapidly making the exact DOS value uncertain. Also V_3Au is an exception in that its experimental T_c is much too low to follow the trends for the other compounds. Several indications such as the calculated very high exchange enhancement suggest that spin fluctuations are the likely mechanism which reduce its T_c. This compound is a good candidate for studying spin fluctuations, since it still has an observable T_c and its electronic specific heat and magnetic susceptibility show strong variation with heat treatment and structural order. The compounds V_3Pt and Nb_3Au are quite well described without assuming strong spin fluctuations.

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