Superconducting Properties of *A*15 Compounds Derived from Band-Structure Results

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Calculations of the electron-phonon interaction, λ, and T_c are presented for ten different *A*15 compounds, V_3X and Nb_3X, X = Al, Ga, Si, Ge, and Sn. The calculated temperature-dependent magnetic susceptibility of Nb_3Sn is also shown to be in good agreement with experiment. We argue that the low-temperature anomalies in many *A*15 materials are related to the very sharp structure in the density of states near the Fermi energy found in our *ab initio* band-structure results.

There has been great interest in the *A*15 materials for more than two decades, primarily due to the high superconducting transition temperatures (T_c) and other unusual electrical and mechanical properties exhibited by many of them.[1] In recent years the advent of sophisticated numerical techniques for calculating the electronic structure of *A*15 compounds has enabled a number of groups to relate some of the properties of the *A*15's to the electronic band structure in a relatively first-principles manner.[2-7]

We have recently done a comprehensive set of *ab initio*, self-consistent, augmented plane-wave (APW) calculations for ten different *A*15 compounds: V_3X and Nb_3X, with X = Al, Ga, Si, Ge, and Sn.[5] In this Letter we report on calculations of the magnetic susceptibility, electron-phonon interaction, and T_c for these materials. We show that a good quantitative understanding of many of the anomalous properties of the *A*15's can be derived from our band-structure results without additional assumptions regarding quasi one-dimensionality, or resort to model density-of-states singularities.

All of our APW band-structure calculations have been done using a warped–muffin-tin approach (fully general treatment of the potential outside of the nonoverlapping APW spheres), and include relativistic effects (neglecting spin-orbit coupling), all self-consistently.[5] The bulk of the calculations were performed using the local density-functional form of exchange correlation, although additional calculations were done using other local exchange approximations to check the sensitivity of our results to exchange. None of the results reported here are qualitatively exchange-approximation sensitive, although details of the Fermi surfaces, for instance, are.

The first question we address is whether our band-structure and density-of-states results can reproduce the unusual temperature dependences of the magnetic susceptibilities, elastic constants, etc., for the *A*15's. To illustrate the success of our approach we show in Fig. 1 our calculated magnetic susceptibility of Nb_3Sn along with the experimental results of Reywald *et al.*[8] The calculations are in excellent quantitative agreement with experiment, and are based on the formulas[9]

$$\chi(T)=\chi_{orb}+\chi_p(T)/[1-\mu F(T)], \qquad (1)$$

$$F(T)=\chi_p(T)/\chi_p(0), \qquad (2)$$

where χ_{orb} is a temperature-independent orbital susceptibility, μ is a Coulomb interaction parameter, and $\chi_p(T)$ is the temperature-dependent Pauli susceptibility. For the fit shown in Fig. 1 we have used the values 0.989×10^{-6} emu/g and

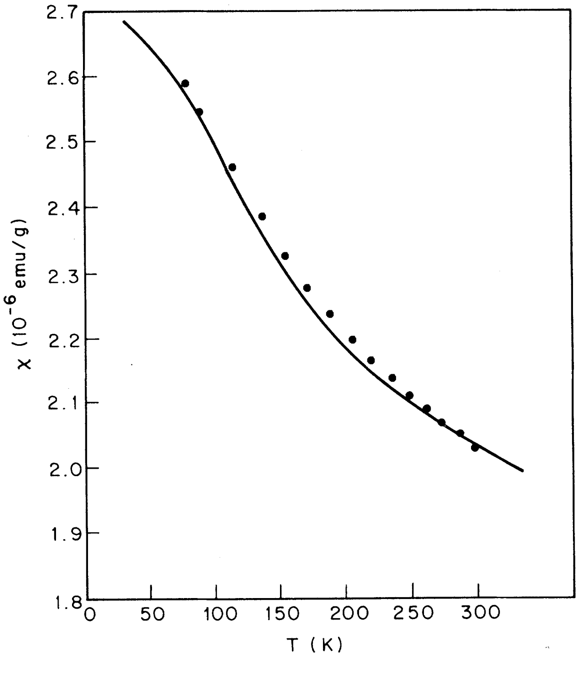

FIG. 1. Calculated magnetic susceptibility of Nb_3Sn (solid curve) and experimental results (dots) from Ref. 8.

0.695 for $\chi_{\rm orb}$ and μ, respectively. These are reasonable values for these quantities. For instance, we find a value of $\mu^* = 0.1-0.2$ using the Morel-Anderson formula,[10] our fitted values of μ, and typical values of the $A15$ d-band width (~ 0.2 eV) and average phonon frequencies (~ 200 K). Our $\chi(T)$ results are in significantly better quantitative agreement with experiment than those of van Kessel, Myron, and Mueller.[6]

The strong temperature dependence of $\chi(T)$ (and presumably of the elastic constants) results from a rapid variation of $N(E)$, the density of states, near the Fermi energy $E_{\rm F}$. This variation is approximately 50% in a 1-mRy (~ 150 K) range around $E_{\rm F}$. Similar good agreement is found for V_3Si and V_3Ga. The compounds without sharp structure in $N(E)$ near $E_{\rm F}$ (e.g., V_3Al, V_3Ge, V_3Sn, Nb_3Al, and Nb_3Ga) do not exhibit strongly temperature-dependent susceptibilities either theoretically or experimentally.[1] We emphasize that these conclusions follow from our first-principles-derived $N(E)$, and do not depend on model density-of-states functions. Our *ab initio* band-structure calculations seem fully able to account for the existence or absence of anomalies in the $A15$ compounds.

We have also calculated the electron-phonon interactions η_A and η_B, and mass enhancement factors λ, using the Gaspari-Gyorffy theory,[11] and the assumption of decoupling the contributions from the A and B sites in the A_3B $A15$ compounds.[12] Results are shown in Table I, along with the T_c values calculated using the Allen-Dynes expression[13] and the phonon density of states of Schweiss *et al.*[14] In all cases $\eta_B \lesssim 0.01\eta_A$ for the $A15$ compounds—electron-phonon scattering from the B site is very ineffective.[15] Since the calculated phonon moments are somewhat crude estimates, there are potential errors of ~ 10% for λ and ~ 20% for T_c.

A theoretical estimate of the $A15$ specific-heat γ values can be made using our calculated values of $N(E_{\rm F})$ and λ. On comparing these results with the various experimental values, in several cases we find discrepancies of more than 25%. Similar comparisons for other transition-metal compounds and elements often yield similar discrepancies. We feel that the origin of this disagreement deserves further study.

A striking result is the prediction of relatively low values of $N(E_{\rm F})$, η, λ, and T_c for both Nb_3Ge and Nb_3Si (for three different lattice constants, 5.03, 5.10, and 5.20 Å). Both λ and T_c were determined for these compounds using estimated values of the Nb-site phonon moments from the experimental results for Nb_3Sn.[14] The observed high T_c values for Nb_3Ge, in excess[16,17] of 23 K in relatively thin film samples, can be reconciled with our results only if there is unusual phonon softening in this material or if there is some other unusual property such as defects or surface phonon effects which somehow enhance T_c in these samples. Experimental information on the phonon spectrum of Nb_3Ge is especially important in order to solve this puzzle. We remark that experimentally measured x-ray photoelectron

TABLE I. Electronic density of states at the Fermi level, $N(E_{\rm F})$ [states/Ry-(unit cell) for two spins]; electron-phonon interactions for the A and B sites, η_A and η_B (ev/A^2); calculated and measured (by inverting the McMilan-type equation of Ref. 13) mass enhancement factors λ; and calculated and measured values of T_c. The value $\mu^* = 0.13$ was used throughout.

	$N(E_{\rm F})$	η_A	η_B	$\lambda^{\rm calc.}$	$\lambda^{\rm expt.}$	$T_c^{\rm calc.}$	$T_c^{\rm expt.}$
V_3Al	188.9	6.87	0.03	1.09	0.87	14.8	9.6
V_3Ga	266.7	9.26	0.05	1.48	1.17	23.0	16.5
V_3Si	200.2	8.90	0.07	1.18	1.12	18.4	17.1
V_3Ge	114.7	5.04	0.05	0.67	0.70	5.3	6.1
V_3Sn	123.0	3.89	0.04	0.52	0.61	1.9	3.8
Nb_3Al	199.2	13.40	0.05	2.14	1.60	25.1	18.6
Nb_3Ga	191.8	11.91	0.13	1.92	1.74	22.5	20.3
Nb_3Si ($a_0 = 5.03$ Å)	61.42	4.90	0.05	0.65		3.5	
Nb_3Si ($a_0 = 5.10$ Å)	69.20	4.83	0.05	0.64	> 1.0	3.4	> 10
Nb_3Si ($a_0 = 5.20$ Å)	83.61	4.84	0.05	0.64		3.4	
Nb_3Ge	106.7	6.70	0.07	0.89	1.80	8.2	23.2
Nb_3Sn	158.6	8.49	0.06	1.12	1.44	12.6	18.0

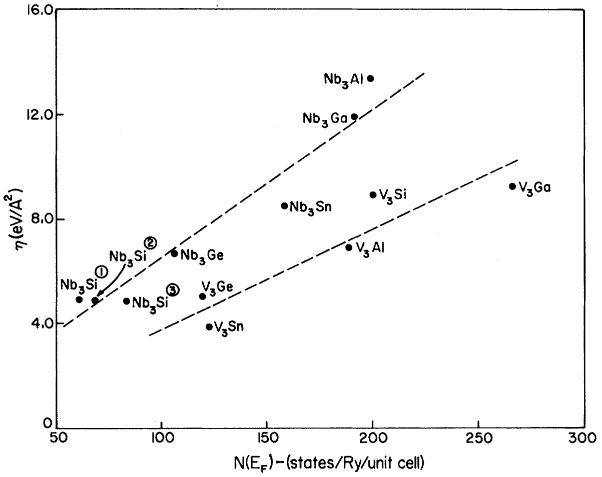

FIG. 2. Calculated electron-phonon interaction $\eta = N(E_F)\langle I^2\rangle$ vs electronic density of states for ten $A15$ compounds (three lattice constants for Nb_3Si, see text).

spectra[18] and recent specific heat measurements[19] for Nb_3Ge appear to support our result that Nb_3Ge is a relatively low-density-of-states $A15$ material. The experimental results of Somekh and Evetts,[20] who obtained T_c enhancements of nearly 5 K for V_3Ge by sputtering, also indicates that there is still much to be understood regarding the physics of thin-film samples of $A15$ materials. We also note that the above arguments apply equally well to our results for Nb_3Si.

Our results for T_c for Nb_3Sn in Table I show that our calculations underestimate λ by ~20% for this compound. Recent tunneling measurements by Moore, Beasley, and Rowell[21] show that there is a significant enhancement of the tunneling density of states, $\alpha^2(\omega)F(\omega)$, at low frequencies compared with the phonon density of states, $F(\omega)$. This would indicate that we may be overestimating $\langle\omega^2\rangle$ in the denominator in the expression for λ for Nb_3Sn, and would account for our underestimation of λ.

We note that our $N(E_F)$ value for Nb_3Ge differs considerably from those of Arbman and Jarlborg[4] and of Allen *et al.*[22] This accounts for the different calculated values of T_c for Nb_3Ge between our results and Ref. 4. We believe that our techniques for calculating $N(E)$ for the $A15$ materials for a *given band structure* are the most accurate currently available.[5,23] Additional discrepancies are due to the different *band-structure approximations* made by the different groups (see Ref. 5 for a discussion of the different band-structure techniques).

As a last point we show in Fig. 2 a plot of η vs $N(E_F)$ for the $A15$ materials. Very approximately the vanadium- and niobium-based compounds fall into two families, with $\eta_{Nb_3B} > \eta_{V_3B}$. Although the relationship $\eta \propto N(E_F)$ is qualitatively obeyed, there is a good deal of scatter. This could be real, or may be related to uncertainties (~10%) in our calculated $N(E_F)$.

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Temperature-Dependent Single-Ion Excitations in Anisotropic Paramagnets

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By an exact calculation for an Ising chain it is established that single-ion (electronic) energy levels are temperature dependent in anisotropic paramagnets. The effect is produced by developing anisotropic spin-spin correlations and, in a more general context, is investigated using the correlated–effective-field statistical approximation. It should be directly observable by spectroscopic means in strongly anisotropic paramagnetic systems.

Most crystal-field–split electronic excitations involving magnetic ions in concentrated magnetic systems are dispersionless.[1] They can therefore be thought of as effective "single-ion" excitations. The exceptions are those which involve levels possessing nonzero matrix elements of exchange energy with thermally populated states.[2-7] Although optical spectra dominantly contain modes in the latter category (at least in absorption) the gross effects of magnetic order upon them are in fact often well accounted for by simple (dispersionless) molecular-field theory,[8,9] due presumably to the relative smallness of the relevant matrix elements for these cases. In this picture, the single-ion excitations are shifted or split by the internal molecular field in an ordered magnetic phase, but become temperature independent above the ordering temperature where this internal field averages to zero. To my knowledge this temperature independence for paramagentic phases is still commonly assumed and no more accurate theoretical discussion has ever been presented. Experimental evidence for paramagnetic line shifts is scant, but I have found one paper[10] which claims such an observation in $Dy_3Al_5O_{12}$.

In this Letter I establish by an exact calculation for an Ising linear-chain model that single-ion energy gaps can indeed be significantly temperature dependent in a disordered anisotropic magnetic system. In a more general context I note that the correlated–effective-field (CEF) theory of magnetism[11] suggests that this temperature dependence is present in all paramagnetic systems which possess uniaxial or lower magnetic anisotropy although the effect may be small unless that anisotropy is marked. The effect is produced by developing anisotropic spin correlations as temperature is lowered and the CEF theory appears, by comparison with the exact results in the Ising chain limit, to be an adequate approximation in most physical situations.

Consider first a spin-1 closed Ising linear chain with single-ion anisotropy, described by the Hamiltonian

$$\mathcal{H} = \sum_{n=1}^{N} [D(S_n^z)^2 - 2JS_n^z S_{n+1}^z], \qquad (1)$$

where spin quantum number $S=1$, number of spins $N \to \infty$, and $S_{N+1}^z \equiv S_1^z$. Regrouping the terms in the form

$$\mathcal{H} = \sum_{n=1}^{N} [\tfrac{1}{2}D(S_n^z)^2 + \tfrac{1}{2}D(S_{n+1}^z)^2 - 2JS_n^z S_{n+1}^z], \qquad (2)$$

one notes that the partition function Z can be expressed in S^z representation as

$$Z = \mathrm{tr} \prod_{n=1}^{N} V_n, \qquad (3)$$

in which all the matrices V_n have an identical Hermitian form

$$V_n = V = \begin{pmatrix} e^{-\beta(D-2J)} & e^{-\beta D/2} & e^{-\beta(D+2J)} \\ e^{-\beta D/2} & 1 & e^{-\beta D/2} \\ e^{-\beta(D+2J)} & e^{-\beta D/2} & e^{-\beta(D-2J)} \end{pmatrix}, \qquad (4)$$

where $\beta = 1/kT$ and the product Π implies simple matrix multiplication.

By a unitary transformation $V' = \mathcal{S}^{-1} V \mathcal{S}$ the matrix V can be diagonalized in the form

$$V' = \begin{pmatrix} z & 0 & 0 \\ 0 & z_+ & 0 \\ 0 & 0 & z_- \end{pmatrix}, \qquad (5)$$