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Electronic structure of $ZnCNi_3$

M. D. Johannes[1,2] and W. E. Pickett[1]
[1]*Department of Physics, University of California, Davis, California 95616, USA*
[2]*Code 6391, Naval Research Laboratory, Washington, D.C., USA*

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According to a recent report by Park *et al.*, $ZnCNi_3$ is isostructural and isovalent to the superconducting ($T_c \sim 8$ K) antiperovskite, $MgCNi_3$, but shows no indication of a superconducting transition down to 2 K. A comparison of calculated electronic structures shows that the main features of $MgCNi_3$, particularly the van Hove singularity near the Fermi energy (E_F), are preserved in $ZnCNi_3$. Thus, the reported lack of superconductivity in $ZnCNi_3$ is not explainable in terms of T_c being driven to a very low value by a small Fermi level density of states. We propose that the lack of superconductivity, the small value of the linear specific heat coefficient γ and the discrepancy between theoretical and experimental lattice constants can all be explained if the material is assumed to be a C-deficient α-$ZrCNi_3$ similar to the analogous nonsuperconducting phase of $MgCNi_3$.

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I. INTRODUCTION

The appearance of superconductivity[1] near 8 K in the Ni-rich perovskite, $MgCNi_3$, has stimulated much interest not only because it is unusual in a compound that is primarily Ni, but because the exact nature of the superconducting state and its microscopic origins are still being debated. Like another unusual superconductor, MgB_2, it has so far resisted efforts to increase the critical temperature significantly by chemical substitution. Both Cu and Co doping on the Ni site reduce the critical temperature (T_c), predictably due to band effects (electron doping) in the former case and possibly due to spin fluctuations in the latter.[2,3] The transition temperature can be raised by 1 K through Ni-site doping[3] with Fe, but this temperature occurs in $MgCNi_{3-x}Fe_x$ with $x=0.05$, and any further doping again reduces T_c. Mg deficiencies or excesses have some effect on the sharpness and onset of the superconducting transition, but the optimal composition still results[4,5] in a maximum T_c of 8 K. The superconductivity of $MgCNi_3$ seems most sensitive to the carbon site occupancy. Boron doping on the carbon site[5] reduces T_c for relative B/C concentrations of up to 0.07 and eliminates superconductivity for any greater concentration. MgC_xNi_3 with $x<1.0$ remains a cubic perovskite but undergoes an isostructural transition[1,5] to a smaller volume α phase that no longer superconducts.

Recently the synthesis of $ZnCNi_3$ has been reported by Park *et al.*[6] Since $ZnCNi_3$ is very similar to $MgCNi_3$ structurally, and (as we will show) electronically, the lack of a superconducting transition down to 2 K is quite unexpected. Understanding why superconductivity is seen in one compound but not the other could be important in resolving remaining questions about the unusual behavior of $MgCNi_3$. The experimental data suggest[6] that a strongly depressed density of states (DOS) (compared to $MgCNi_3$) at the Fermi level (E_F) could be responsible for pushing the transition temperature of $ZnCNi_3$ below 2 K. The results of a careful comparison of the electronic structure of the two compounds are presented here, and the required lowering of the DOS is shown to be absent. Because the reported lattice constants differ by 4%, we calculate the theoretical equilibrium lattice constants and explore the effects of pressure on the electronic structure of each material. We find that discrepancies when compared to $MgCNi_3$ in DOS, in lattice constant, and in observations of superconductivity can be understood if the reported $ZnCNi_3$ samples are C-deficient α phase as are $MgCNi_3$ samples with C deficiency.

II. CALCULATIONAL METHODS AND ELECTRONIC STRUCTURE

$ZnCNi_3$ has the typical ABO_3 cubic perovskite structure, but with the oxygen atoms on the faces replaced by Ni atoms. As Zn and Mg both have a formal valency of 2^+, $ZnCNi_3$ is isovalent as well as isostructural with $MgCNi_3$, both residing in space group 221 ($Pm\overline{3}m$). Calculations were carried out using Wien2k,[7] a full-potential, augmented plane wave + local-orbital (APW+lo) method, and with the local density approximation of Perdew and Wang[8] to the exchange-correlation potential. The density is well converged with 816 k-pts in the irreducible Brillouin zone. The sphere radii used were 2.1 a.u. for Zn/Mg, and 1.72 a.u. for both C and Ni; Rkmax was set to 7.00 resulting in ~ 600 APWs and 50 local orbitals. The experimental lattice constants were used in the initial calculations for both $MgCNi_3$ ($a=3.81$ Å) and $ZnCNi_3$ ($a=3.66$ Å). Compression and expansion percentages are given in terms of these experimental values.

The electronic structure of $MgCNi_3$ has been presented previously by several groups.[9–12] The dominant feature is a remarkable, sharp van Hove singularity 65 meV below E_F, which was traced to an extremely flat band around the M point $(=(1,1,0)\pi/a)$ of the Brillouin zone. The electronic structure of $ZnCNi_3$ is very similar to that of $MgCNi_3$. The sharp peak just below the Fermi energy is still dominant, though it is shifted slightly downward in energy by approximately 30 meV and has broadened somewhat (Fig. 1, top

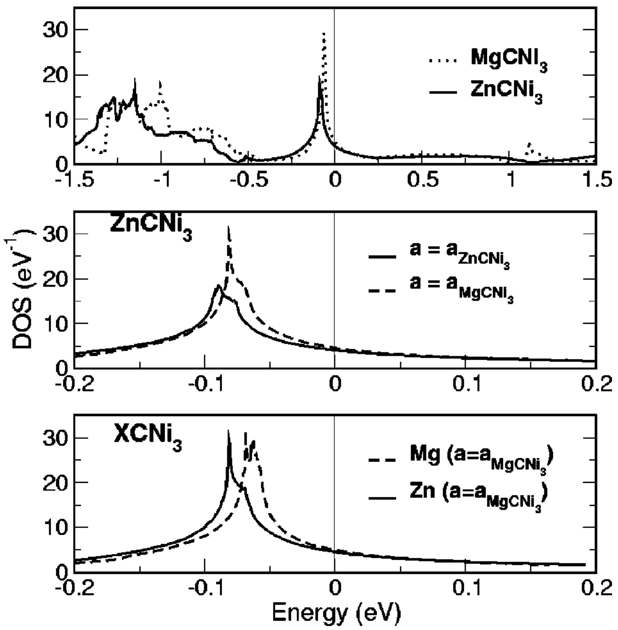

FIG. 1. Top panel: $ZnCNi_3$ and $MgCNi_3$ at their reported equilibrium lattice constants. Middle panel: $ZnCNi_3$ at its own experimental lattice constant and at that of $MgCNi_3$. The effect of pressure at E_F is small. Bottom panel: $MgCNi_3$ and $ZnCNi_3$ both at the same lattice constant (reported value for $MgCNi_3$). Differences in electronic structure are larger than can be accounted for by pressure alone, though still small.

panel). In both compounds, the Ni ions are twofold coordinated with their nearest neighbors, the coplanar C ions. Hybridization between Mg/Zn and Ni ions is very small, consistent with the very similar electronic structures of the two compounds. The dispersion created by the two-dimensional bonding of Ni-*d* and C-*p* orbitals is responsible[9,10] for the nearly dispersionless band centered on M. In $ZnCNi_3$, the situation is much the same, but the 4*p* states of the Zn ions, with which the Ni ions are fourfold coordinated, do participate weakly in the bonding states near the Fermi energy. This weak bonding is three dimensional, accounting for the slightly increased dispersion around the M point as well as the lowered energy of the DOS peak.

The downward shift of the peak has the effect of reducing the DOS at the Fermi energy $[N(0)]$, with respect to that of $MgCNi_3$, by about 1 eV^{-1}, i.e., by about 20%. This decrease relative to the Mg compound is much less than what is necessary to account for the lack of superconductivity through conventional Bardeen-Cooper-Schrieffer (BCS) theory (see Sec. II B).

A. Pressure dependencies and bulk modulus

Expansion of the $ZnCNi_3$ lattice narrows the peak and brings it nearer the Fermi level (Fig. 1 middle panel) that is, expansion makes it more $MgCNi_3$-like. This has the effect of raising the DOS at the Fermi energy, but the change is very small even for fairly large expansions. In $ZnCNi_3$, an expansion of $\sim$12% by volume caused a change in the DOS of only 10%. $MgCNi_3$ seems to be even slightly *less* sensitive than this. A calculation of $ZnCNi_3$ at the experimental lattice constant of $MgCNi_3$ shows, however, that the differences in the electronic structures of the two compounds are due to more than simply volume. (See bottom panel of Fig. 1.) The probable source of the small differences in electronic structure is residual hybridization of Ni-*d* and Zn-*p* orbitals. As the lattice is expanded the overlap between these orbitals decreases, but does not disappear completely. By looking at the orbitally resolved character of the flatband, we have observed that the amount of Zn-*p* character in $ZnCNi_3$, although minor (approximately 5% of the total DOS near E_F), is larger by nearly a factor of 2 than the amount of Mg-*p* character in $MgCNi_3$.

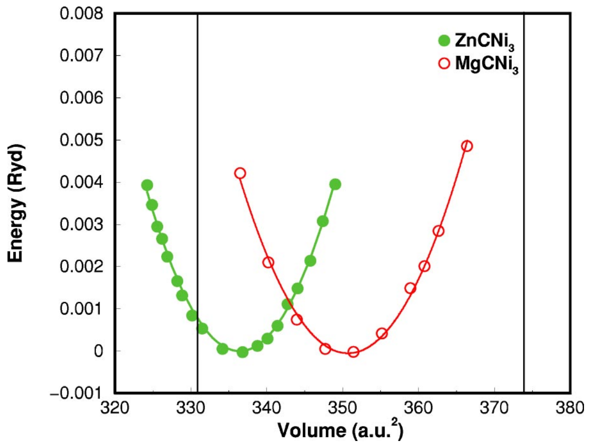

FIG. 2. The bulk moduli and equilibrium volumes of $MgCNi_3$ and $ZnCNi_3$. The experimental volumes are shown as vertical lines —that of $ZnCNi_3$ is smaller than the calculated value.

The calculated equilibrium volume of $ZnCNi_3$ compares very favorably with the reported value, the latter being 0.53% smaller by lattice constant. However, this result is somewhat unusual in that the theoretical value is actually larger than the experimental one. The calculated equilibrium value of $MgCNi_3$ is 2% smaller in lattice constant than the experimental value. The discrepancy is in the more common direction, but slightly larger than usual. The two energy versus volume curves are shown in Fig. 2, along with the experimental volumes. The bulk modulus of $ZnCNi_3$ taken at the theoretical volume is 251 GPa, whereas that of $MgCNi_3$ taken at its own theoretical volume is 214 GPa. The $MgCNi_3$ result is similar to that obtained through linearized muffin-tin orbital calculations.[3] Both these values are obtained by fitting the Murnaghan equation of state[13] to an energy versus volume curve and extracting the bulk modulus through the relation: $B=V\partial^2E/\partial V^2$. The smaller volume Zn compound is, as expected, harder than the Mg compound when the calculated equilibrium volumes are used. However, the bulk moduli of these two compounds, calculated at their respective experimental volumes, differ by only 3.6%, with $MgCNi_3$ being *harder* than $ZnCNi_3$. This is a consequence of finding the theoretical equilibrium value of $ZnCNi_3$ above the reported value, while that of $MgCNi_3$ is below the reported value.

B. Electron-phonon coupling

The empirical value quoted for the electron-phonon coupling constant, λ, in $MgCNi_3$ depends on the method by which it is obtained. Using the size of the jump in specific heat at the superconducting transition and assuming weak coupling BCS behavior yields[1] $\lambda = 0.79$. This method is obviously unavailable for $ZnCNi_3$ since no transition has yet been observed. The constant λ can alternatively be derived by the more common method of comparing experimental and theoretical results for the linear coefficient γ from specific heat data

$$\lambda = \frac{\gamma_{\mathrm{exp}}}{\gamma_{\mathrm{th}}} - 1; \quad \gamma_{\mathrm{th}} = \frac{\pi^2 k_B^2}{3} N(0). \tag{1}$$

There is some variation in the reported values of γ_{exp} for $MgCNi_3$. Some sources[1,6,14] place the value at around 29 mJ/mol K^2 for the zero-field value, while others[15,16] cite a higher value of about 33.5 mJ/mol K^2. Using this range of values, we obtain $\lambda = 1.5-1.75$ for the Mg compound, in agreement with previous results derived in this way.[9,17] However, using this methodology, a negative λ results for $ZnCNi_3$, due to the small $\gamma_{\mathrm{exp}} = 6.77$ reported,[6] less than 25% of that of $MgCNi_3$. This unphysical result highlights the discrepancy between experimental and theoretical comparisons of these two compounds. Large differences in observed specific heat data combined with very small differences in calculated electronic structure properties produce this unphysical value for λ (see Table I).

Furthermore, it is the ratio of the γ's from the two different compounds that stipulates that the DOS of the $ZnCNi_3$ sample must be significantly lower than that of $MgCNi_3$. Park *et al.*[6] use the definition in Eq. (1) along with their specific heat data to put an upper bound on the value of the DOS of the Zn compound relative to that of the Mg compound at the Fermi level

$$\frac{\gamma_{\mathrm{Mg}}}{\gamma_{\mathrm{Zn}}} = \frac{N(0)_{\mathrm{Mg}}(1+\lambda_{\mathrm{Mg}})}{N(0)_{\mathrm{Zn}}(1+\lambda_{\mathrm{Zn}})}. \tag{2}$$

It is clear from this equation that $N(0)_{\mathrm{Zn}}$ takes its greatest value when $\lambda_{\mathrm{Zn}} = 0$. The ratio then yields $N(0)_{\mathrm{Zn}} \leqslant 0.41\ N(0)_{\mathrm{Mg}}$. As mentioned above, there is no such large depression of the $ZnCNi_3$ DOS as compared to the $MgCNi_3$ DOS at the Fermi level. In fact, our calculated value of $N(0)_{\mathrm{Zn}}$ exceeds the derived upper bound by almost a factor of 2.

III. DISCUSSION

$MgCNi_3$ has now been studied fairly extensively, and we review some results that may be relevant. According to Ren *et al.*,[5] the carbon occupancy of $MgCNi_3$ is sensitive to preparation conditions and two different phases of the compound emerge. The α phase is carbon depleted, while the β phase is nearly stoichiometric (carbon occupancy is 0.96). Both α and β phases share the same cubic space group, but the α phase lattice parameter is 1.3% smaller and, unlike the β phase, it does not superconduct. This is consistent with previous studies[18] which found that T_c decreases linearly with decreasing carbon concentration until eventually, at a carbon occupancy of around 0.88–0.89, a multiphase region is reached in which bulk superconductivity no longer exists. The reported α phase occurred at an occupancy of 0.75 at the carbon site,[5] well within this multiphase region. Shan *et al.*[16] found that the specific heat γ was 50% lower in the α phase than in the β phase. The α phase can then be distinguished from the β phase in three important aspects: it does not superconduct, it has a significantly smaller γ, and its equilibrium lattice constant is 1.3% smaller.

TABLE I. Comparison of $MgCNi_3$ and $ZnCNi_3$ (experimental values taken from Park [6] *et al.*). See text for discussion of unphysical λ value.

	$N(0)\mathrm{ev}^{-1}$	γ_{exp} mJ/mol K^2	$\Theta_D K^2$	λ
$MgCNi_3$	5.003	29.50	255.9	1.5
$ZnCNi_3$	4.049	6.77	421.3	−0.29

Most if not all of the evidence regarding $ZnCNi_3$ can be reconciled if we suppose that the phase reported by Park *et al.* is a carbon deficient "α-$ZnCNi_3$" phase corresponding to α-$MgCNi_3$. The electronic structure of the two compounds is so similar that it is reasonable to assume that carbon deficiencies in the Zn structure would have much the same effect as carbon deficiencies in the Mg structure. Assuming that the experimental results for this compound were taken from an α phase of $ZnCNi_3$, all discrepancies between theory and experiment discussed in this paper disappear. A 1.3% increase in the lattice parameter would result in the common situation in which the theoretical value is smaller than the experimental one. If γ is multiplied by a factor of 2, as it would be in moving from an α to β phase, the λ value calculated using Eq. (1) has a value of 0.42, eliminating the nonphysical negative result. Previous electronic structure calculations show that in $MgCNi_3$, N(0) decreases dramatically as C concentration decreases,[16] resulting in suppression of the superconducting transition. Similar effects would be expected for $ZnCNi_3$.

Another striking difference in the data between the Zn and Mg based compounds is a sharply increased lattice stiffness Θ_D. Even in the minimally doped alloy $Mg_{0.85}Zn_{0.15}CNi_3$, an increase of 38% was observed[19] for Θ_D and in the fully Zn substituted compound, the increase is 67%.[6] The addition of Zn in any concentration causes a volume contraction and a concurrent hardening of phonon modes in general. In pure $MgCNi_3$, the frequency of a very soft acoustic Ni-based phonon mode is calculated in the harmonic approximation to become negative along much of the $\Gamma - M$ direction of the Brellouin zone.[20,21] Anharmonic stabilization of this mode results in observed dynamic displacements of the Ni ions perpendicular to the Ni–C direction.[21] This "breathing" distortion allows each Ni ion to move away from its two C neighbors and toward the empty interstitial site. In a C deficient compound, stress on the Ni ions would be partially relieved by vacancies, reducing the advantage of such distortions and thereby increasing Θ_D.

IV. CONCLUSIONS

From our calculations, stoichiometric $ZnCNi_3$ and $MgCN_3$ are very much alike in both structural and electronic properties. The experimental report of widely differing specific heat data and the lack of superconductivity down to 2 K seems highly unusual in light of the close similarity of these two compounds. The rather large suppression of the DOS at the Fermi energy required to interpret the experimental results using BCS theory fails to materialize from the calculations. All results are in line with a $ZnCNi_3$ phase that is carbon deficient rather than stoichiometric. Carbon deficient $MgCNi_3$ is known to have a smaller volume than the stoichiometric compound, to have a strongly depressed γ, and to be nonsuperconducting. Our results suggest that the lattice constant of stoichiometric $ZnCNi_3$ is likely to be larger than that which is reported (probably near 3.74 Å), and that a depression of less than 20% in N(0) occurs. In the crude approximation that all other factors are constant, this depression would cause a reduction in T_c of ~50% compared to $MgCNi_3$, still well above the measured threshold of 2 K. Thus, it seems likely that a truly stoichiometric $ZnCNi_3$ compound would be superconducting at only a somewhat lower temperature than $MgCNi_3$.

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