Electronic Structure of ZnCNi$_3$

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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) anti-perovskite, MgCNi$_3$, but shows no indication of a superconducting transition down to 2K. A comparison of calculated electronic structures shows that the main features of MgCNi$_3$, particularly the van Hove singularity near the Fermi energy, 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 $\gamma$ and the discrepancy between theoretical and experimental lattice constants can all be explained if the material is assumed to be a C-deficient $\alpha$-ZrCNi$_3$ similar to the analogous non-superconducting phase of MgCNi$_3$.

I. INTRODUCTION

The appearance of superconductivity 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 the nature of the superconducting state and its microscopic origins are still being debated. Like the other unusual new 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. The transition temperature can be raised by 1 K through Ni-site dopings 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 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 reduces $T_c$ for relative B/C concentrations of up to 0.07 and eliminates superconductivity for any greater concentration. MgC$_2$Ni$_3$ with $x < 1.0$ remains a cubic perovskite but undergoes an isomorphous transition to a smaller volume $\alpha$-phase that no longer superconducts.

Recently the synthesis of ZnCNi$_3$ has been reported by Park et al. 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 suggests 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 $\alpha$-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 (Pmna). Calculations were carried out using Wien2k, a full-potential, augmented plane wave + local-orbital method, and with the local density approximation (LDA) of Perdew and Wang$^6$ 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; the Rkmax was set to 7.00. The experimental lattice constants were used in the initial calculations for both MgCNi$_3$ ($a = 3.81$ A) and ZnCNi$_3$ ($a = 3.66$ A). 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.$^{3,10,11,12}$ 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 ($=(1,1,0)\frac{a}{2}$) 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 panel). In both compounds, the Ni ions are two-fold coordinated with their nearest-neighbors, the co-planar 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 for the nearly dispersionless band centered on M. In ZnCNi$_3$, the situation is much the same, but the 4p states of the Zn ions, with which the Ni ions are four-fold 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 BCS theory (see Section C).

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 equilibrium 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 flat band, we have observed that the amount of Zn-p character in ZnCNi$_3$, although minor, is larger by nearly a factor of two than the amount of Mg-p character in MgCNi$_3$.

FIG. 1: Top panel: ZnCNi$_3$ and MgCNi$_3$ at their reported equilibrium lattice constants. Middle panel: ZnCNi$_3$ at its own lattice constant and at that of MgCNi$_3$. The effect of pressure is rather small. Bottom panel: MgCNi$_3$ and ZnCNi$_3$ both at the same lattice constant (that of MgCNi$_3$). Differences in electronic structure are larger than can be accounted for by pressure alone, though still small.
that of MgCNi$_3$ taken at its own theoretical volume is 214 GPa. The MgCNi$_3$ result is similar to that obtained through LMTO calculations. Both these values are obtained by fitting the Murnaghan equation of state to an energy vs. volume curve and extracting the bulk modulus through the relation: $B = V \frac{\partial^2 E}{\partial V^2}$. The smaller volume Zn compound is, as expected, harder than the Mg compound. 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, $\lambda$, 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 $\lambda = 0.79$. This method is obviously unavailable for ZnCNi$_3$ since no transition has yet been observed. $\lambda$ can alternatively be derived by the more common method of comparing experimental and theoretical results for the linear coefficient $\gamma$ from specific heat data:

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

There is some variation in the reported values of $\gamma_{exp}$ for MgCNi$_3$. Some sources cite a value of about 33.5 mJ/mol K$^2$ for the zero-field value, while others cite a higher value of around 29 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. However, using this methodology, a negative $\lambda$ results for ZnCNi$_3$, due to the small $\gamma_{exp}=6.77$ reported. 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 $\lambda$.

Furthermore, it is the ratio of the $\gamma$'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. 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.

**III. DISCUSSION**

MgCNi$_3$ has now been studied fairly extensively, and we review some results that may be relevant. According to Ren et al., the carbon occupancy of MgCNi$_3$ is sensitive to preparation conditions and two different phases of the compound emerge. The $\alpha$-phase is carbon depleted, while the $\beta$ phase is nearly stoichiometric (carbon occupancy is 0.96). Both $\alpha$ and $\beta$ phases share the same cubic space group, but the $\alpha$ phase lattice parameter is 1.3% smaller and unlike the $\beta$-phase, it does not superconduct. This is consistent with previous studies which found that $T_c$ decreases linearly with decreasing carbon concentration until eventually, at a carbon occupancy of around 0.88-0.89, a multi-phase region is reached in which bulk superconductivity no longer exists. The reported $\alpha$-phase occurred at an occupancy of 0.75 at the carbon site, well within this multi-phase region. Shan et al. found that the specific heat $\gamma$ was 50% lower in the $\alpha$-phase than in the $\beta$-phase. The $\alpha$-phase can then be distinguished from the $\beta$-phase in three important aspects: it does not superconduct, it has a significantly smaller $\gamma$, and its equilibrium lattice constant is 1.3% smaller.

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 “$\alpha$ - ZnCNi$_3$” phase corresponding to $\alpha$-MgCNi$_3$. The electronic structure of the two compounds is similar to that 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 $\alpha$-phase of ZnCNi$_3$, 

|                  | $N(0)$ ev$^{-1}$ | $\gamma_{exp}$ mJ/mol K$^2$ | $\Theta_D$ K | $\lambda$ |
|------------------|-----------------|-----------------------------|--------------|----------|
| MgCNi$_3$        | 5.003           | 29.50                       | 255.9        | 1.5      |
| ZnCNi$_3$        | 4.049           | 6.77                        | 421.3        | -0.29    |

$$\frac{\gamma_M}{\gamma_Zn} = \frac{N(0)_M(1 + \lambda_M)}{N(0)_Zn(1 + \lambda_Zn)}$$

It is clear from this equation that $N(0)_Zn$ takes its greatest value when $\lambda_Zn = 0$. The ratio then yields $N(0)_Zn \leq 0.41 N(0)_M$. 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 $N(0)_Zn$ exceeds the derived upper bound by almost a factor of two.
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 $\gamma$ is multiplied by a factor of two, as it would be in moving from an $\alpha$ to $\beta$ phase, the $\lambda$ value calculated using Eq. 1 has a value of 0.42, eliminating the non-physical negative result. Previous electronic structure calculations show that in MgCNi$_3$, N(0) decreases dramatically as C concentration decreases, resulting in suppression of the superconducting transition. Similar effects would be expected for ZnCNi$_3$.

Another striking difference in the lattice parameter for Ni sites in MgCN$_3$ and MgCN$_2$ is that a depression of less than 20% in N(0) decreases dramatically as C concentration decreases, resulting in suppression of the superconducting transition. Similar effects would be expected for ZnCNi$_3$.

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**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 ZnNi$_3$ phase that is carbon-deficient rather than stoichiometric. Carbon deficient MgNi$_3$ is known to have a smaller volume than the stoichiometric compound, to have a strongly depressed $\gamma$, and to be non-superconducting. Our results suggest that the lattice constant of stoichiometric ZnNi$_3$ 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. A truly stoichiometric ZnNi$_3$ compound would likely be superconducting at only a somewhat lower temperature than MgNi$_3$.

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