

# Suppression of thermopower of $\text{Na}_x\text{CoO}_2$ by an external magnetic field: Boltzmann transport combined with spin-polarized density functional theory

H. J. Xiang<sup>1</sup> and D. J. Singh<sup>2,\*</sup><sup>1</sup>*Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, USA*<sup>2</sup>*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6032, USA*

(Received 10 July 2007; published 13 November 2007)

We calculate the thermopower in  $\text{Na}_x\text{CoO}_2$  using the standard Boltzmann transport theory and first principles electronic structures with spin polarization taken into account. The thermopower is found to be smaller when the system is polarized, which thereby provides an alternative reasonable explanation for the suppression of thermopower in a magnetic field. The role of the spin-orbit coupling on the thermoelectricity is also discussed.

DOI: [10.1103/PhysRevB.76.195111](https://doi.org/10.1103/PhysRevB.76.195111)

PACS number(s): 72.15.Jf, 71.20.-b, 74.25.Fy, 73.50.Jt

## I. INTRODUCTION

Thermoelectric energy conversion is a promising and useful technology for both electric power generation from waste heat and cooling of various electronic devices.<sup>1</sup> The discovery of an unexpectedly large thermopower<sup>2</sup> in  $\text{Na}_x\text{CoO}_2$  led to extensive studies of this system<sup>3,4</sup> and related misfit-layered cobalt oxide systems.<sup>5,6</sup> Moreover, superconductivity with possible unconventional pairing was reported in a hydrated compound,  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$  ( $x=0.35$ ,  $y=1.3$ ).<sup>7</sup>  $\text{Na}_x\text{CoO}_2$  displays a rich phase diagram:<sup>8</sup> a Pauli paramagnetic metal ( $x < 0.5$ ) and a Curie-Weiss metal ( $x > 0.5$ ) separated by a charge-ordered insulator (at  $x=0.5$ ), though recently, it was suggested that the boundary between the two metals is at  $x \sim 0.60$ .<sup>9,10</sup> Thus, the sodium cobalt oxides are currently of great interest from both application and physics points of view.

$\text{Na}_x\text{CoO}_2$  exhibits an unusual combination of transport properties which are conventionally interpreted as either metallic or insulating features. It shows a low metallic resistivity of  $200 \mu\Omega \text{ cm}$  accompanied by a large thermopower about  $100 \mu\text{V/K}$  at room temperature,<sup>2</sup> which is about ten times larger than in typical metals. In particular, thermoelectric figure of merit  $ZT$  exceeds unity above 800 K. Ever since the large thermopower in  $\text{Na}_x\text{CoO}_2$  was discovered by Terasaki *et al.*,<sup>2</sup> its origin has been under debate. The role of spin fluctuations, as in heavy-fermion systems, was suggested in the original report.<sup>2</sup> Koshibae *et al.*<sup>11</sup> proposed a theory for the large thermoelectric power based on the generalized Heikes formula.<sup>12</sup> In their theory, Co  $3d$  electrons are not considered to have extended Bloch states but to be rather localized. The competition between the crystalline field and Hund coupling leads to large degeneracy in the cobalt  $3d$  states. Thus, the thermoelectric power is enhanced due to their large spin entropy. Within the standard Boltzmann transport theory,<sup>13</sup> Singh calculated the thermopower of  $\text{Na}_{0.5}\text{CoO}_2$  using the local density approximation (LDA) band structure.<sup>14</sup> The 300 K value predicted using the low-temperature Boltzmann expression within the constant scattering time approximation is  $S=110 \mu\text{V/K}$ , which is in good agreement with the experimental value. High thermopowers were also found at other doping levels using density functional band structures and Boltzmann transport theory.<sup>15,16</sup>

Meanwhile, Motrunich and Lee interpreted the anomalous thermopower in terms of charge frustration.<sup>17</sup>

It appears that some experimental results support the spin entropy theory. In particular, Wang *et al.* found a suppression of the thermopower in a longitudinal magnetic field at low temperature and argued that the spin entropy is the likely source for the large thermopower.<sup>3</sup> Using the  $t$ - $J$  model, Haerter *et al.* suggested that the field suppression of the thermopower may arise from strong electron correlations.<sup>18</sup> Their results agree with the interpretation in terms of spin entropy as the leading contribution to the field suppression. By investigating the dependence of the thermopower on both magnetic field and temperature, Limelette *et al.*<sup>6</sup> suggested that the thermopower in related misfit cobalt oxides was composed of two components, a kinetic one originating from quasiparticles renormalized by electronic correlations<sup>19</sup> and a spin entropy contribution.

However, there are several difficulties in the spin entropy explanation. First, the generalized Heikes formula was proposed for the calculation of the thermopower in a system of interacting localized carriers with hopping conduction.<sup>12</sup> In contrast,  $\text{Na}_x\text{CoO}_2$  displays metallic behavior even below 4 K.<sup>2,4</sup> This was noticed before by Takeuchi *et al.*<sup>20</sup> Second, the Heikes formula for the thermopower is derived within the high-temperature limit ( $t \ll k_B T$ , where  $t$  and  $T$  denote hopping parameter and temperature, respectively). However, the relevant energy scales, Fermi energy, hopping parameters, band width, etc.,<sup>14,21</sup> are much greater than  $k_B T \approx 26 \text{ meV}$ , i.e., in the opposite limit, and in fact, the thermopower is strongly  $T$  dependent. Here, the dependence of the thermopower on the magnetization is explored using standard Boltzmann transport theory combined with the first principles electronic structure. We find thermopowers in accord with experimental data without the addition of any extra spin entropy, and in addition find a strong decrease upon magnetization. The implication is that both the high thermopower and its partial suppression in high fields can be understood using conventional transport theory applicable to other thermoelectric materials, and that the unique thermoelectric properties of  $\text{Na}_x\text{CoO}_2$  are due to its unusual band structure as opposed to strong correlation effects.

## II. BAND STRUCTURE CALCULATIONS AND BOLTZMANN TRANSPORT

According to the Boltzmann transport theory,<sup>13</sup> the thermopower  $S$  can be written as

$$S = \frac{1}{eT} \left( \frac{eL^{12} + \mu L^{11}}{L^{11}} \right), \quad (1)$$

where  $\mu$  is the chemical potential and  $e$  represents the charge of an electron. The generalized transport coefficients  $L^{11}$  and  $L^{12}$  can be calculated as

$$L_{\alpha\beta}^{11}(T, \mu) = \frac{-e^2}{\Omega} \int d^3\tilde{\mathbf{k}} \tau(\tilde{\mathbf{k}}) v_{\alpha}(\tilde{\mathbf{k}}) v_{\beta}(\tilde{\mathbf{k}}) \frac{\partial f_{\mu}(T, \epsilon(\tilde{\mathbf{k}}))}{\partial \epsilon(\tilde{\mathbf{k}})},$$

$$L_{\alpha\beta}^{12}(T, \mu) = \frac{1}{e\Omega} \int d^3\tilde{\mathbf{k}} \tau(\tilde{\mathbf{k}}) v_{\alpha}(\tilde{\mathbf{k}}) v_{\beta}(\tilde{\mathbf{k}}) \epsilon(\tilde{\mathbf{k}}) \frac{\partial f_{\mu}(T, \epsilon(\tilde{\mathbf{k}}))}{\partial \epsilon(\tilde{\mathbf{k}})}, \quad (2)$$

and we note that  $L^{11}$  is, in fact, the conductivity  $\sigma$ . When the system is spin polarized, the two-current model<sup>22</sup> in which the spin-flip scattering is neglected can be used to calculate  $L^{11}$  and  $L^{12}$ :

$$\begin{aligned} L^{11} &= L^{11}(\uparrow) + L^{11}(\downarrow), \\ L^{12} &= L^{12}(\uparrow) + L^{12}(\downarrow), \end{aligned} \quad (3)$$

where  $L(\uparrow)$  and  $L(\downarrow)$  are computed using the spin up and down band structures, respectively. Direct coupling of the thermopower to magnetic field via an energy dependent normal magnetoresistance is not included. This would be a very small effect. One can easily verify that this gives the same result as that from the conventional formula when dealing with a non-spin-polarized (NSP) system. Within the constant scattering time approximation [ $\tau(\tilde{\mathbf{k}}) = \tau$ ],<sup>23,24</sup> the thermopower can be obtained directly from the band structure without any adjustable parameters.

Our LDA calculations are performed by using the full-potential linearized augmented plane waves plus local orbital method<sup>25</sup> as implemented in the WIEN2K code.<sup>26</sup> Nonoverlapping sphere radii of 2.27, 1.88, and 1.67  $a_0$  are used for the Na, Co, and O atoms, respectively. The value of  $R_{MT}^{min} K_{max}$  is set to 7.0. Transport properties are sensitive to the Brillouin zone sampling. A dense grid of approximately 22 000  $\mathbf{k}$  points in the zone is used to obtain convergence. Since the concentration of the Na doping of the sample used in the experiment<sup>3</sup> is about 0.68, we mainly focus on  $\text{Na}_{0.68}\text{CoO}_2$ .<sup>27</sup> The virtual crystal approximation is used to simulate the Na doping. To calculate the band structure with different magnetizations, the fixed spin moment (FSM) method<sup>28</sup> is used to constrain the total spin moment. For the calculations of the derivatives and Fermi surface integrals necessary for the transport coefficients, we use the BOLTZTRAP program.<sup>29</sup> Thus, the results presented here are based on Boltzmann transport theory as applied to the self-consistent band structures for  $x=0.68$ . For the magnetization dependence of the thermopower, we used self-consistent band structures as a function of magnetization.

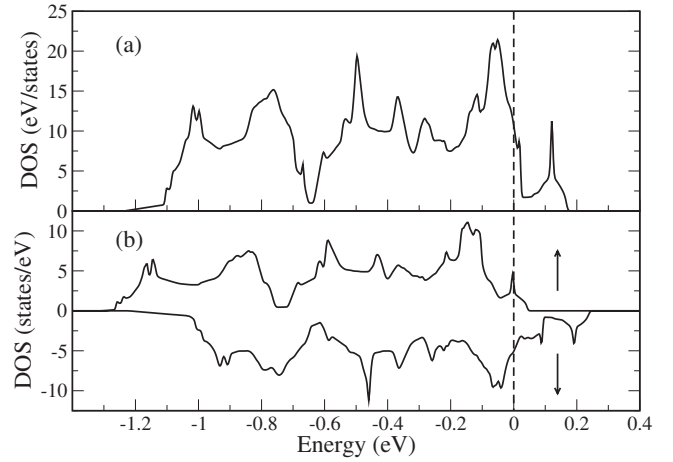


FIG. 1. Calculated electronic density of states of  $\text{Na}_{0.68}\text{CoO}_2$  with (a)  $M=0.00 \mu_B$  and (b)  $M=0.48 \mu_B$ .

The band structure of  $\text{Na}_x\text{CoO}_2$  as calculated within the LDA shows two types of Fermi surfaces: large  $\Gamma$ -centered  $a_g$  hole pockets, which are also seen in photoemission measurements, and a set of small  $e'_g$  pockets, which have not been observed in photoemission experiments.<sup>30–34</sup> It has been argued that small band shifts due to correlations or some other effect may remove the small surfaces, and also that disorder in actual  $\text{Na}_x\text{CoO}_2$  may make them difficult to observe in photoemission.<sup>43</sup> These sections are removed in electronic structure calculations when Coulomb correlations are included in the static LDA+ $U$  approach.<sup>35,36</sup> However, the application of this approach to metals is questionable,<sup>37,38</sup> and in fact, while it removes the  $e'_g$  pockets, it also broadens the entire  $t_{2g}$  manifold, degrading agreement with photoemission and optical measurements in this regard.<sup>39,40</sup> In metals, fluctuations, including charge and orbital fluctuations, are favored by kinetic energy considerations and the presence of  $e'_g$  sections would open more degrees of freedom for fluctuations. Inclusion of on-site Coulomb repulsion within the framework of the dynamical mean field theory, which in addition to the static repulsion in the LDA+ $U$  method also includes local dynamical effects, and is more justified for metals, produces this effect—an increase in the size of the small pockets, accompanied by a narrowing of the  $t_{2g}$  manifold, opposite to the results of LDA+ $U$  calculations.<sup>41,42</sup> In any case, because of the occurrence of  $\langle v_F^2 \rangle$  in the expressions for conductivity, and thermopower, these small pockets do not contribute significantly to transport except perhaps as a source of scattering. Here, we use the LDA band structure, which yields good agreement with experimental thermopowers for this material.

The space group of  $\text{Na}_x\text{CoO}_2$  is  $P6_3/mmc$  in which each unit cell contains two Co ions. The saturated magnetization of  $\text{Na}_x\text{CoO}_2$  is  $2(1-x)$  per unit cell. We show the  $t_{2g}$  density of states (DOS) of  $\text{Na}_{0.68}\text{CoO}_2$  with  $M=0.48 \mu_B$  from the FSM calculation in Fig. 1. For comparison, the DOS of the NSP state ( $M=0 \mu_B$ ) is also plotted. The DOS of the NSP state is similar to that of  $\text{Na}_{0.5}\text{CoO}_2$  (Ref. 14) except for a Fermi level shift due to a higher Na concentration. When there is a finite spin polarization, the spin up and down bands

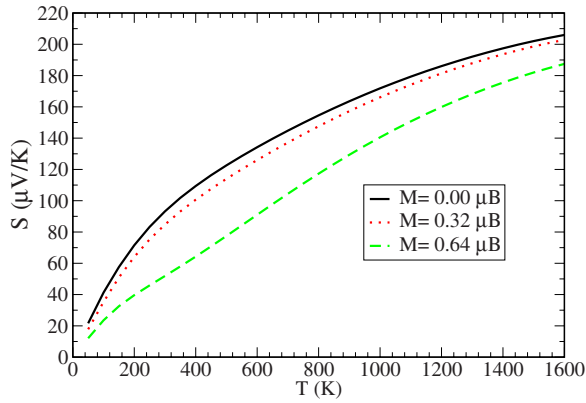


FIG. 2. (Color online) Temperature dependence of thermopower in  $\text{Na}_{0.68}\text{CoO}_2$  with different magnetizations.

shift downward and upward, respectively. The shape of DOS differs slightly from that within the rigid band approximation. In addition, the DOS value at the Fermi level for the spin down component is larger than that for the spin up component.

The bands of  $\text{Na}_x\text{CoO}_2$  are highly anisotropic with much less dispersion along the  $c$  direction.<sup>14</sup> Transport measurements showed much lower conductivity in the  $c$  direction than in the plane and single crystal  $\text{Na}_x\text{CoO}_2$  have the best thermoelectric performance for current in the  $ab$  plane.<sup>2</sup> Because of this, we concentrate on the in-plane thermoelectric property of  $\text{Na}_{0.68}\text{CoO}_2$ . Figure 2 shows the dependence of the in-plane thermopower on the temperature and magnetization. As expected, we can see that for a given magnetization, the thermopower increases with temperature. For the NSP state, both the temperature dependence and the value of thermopower are in surprisingly good agreement with the experimental results:<sup>3</sup> our calculated thermopower values at 100, 200, and 300 K are 40.4 (40), 70.7 (70), 92.3 (90)  $\mu\text{V}/\text{K}$  (values in parentheses are experimental results). This close agreement is probably partly fortuitous since agreement at 10%–20% level is more typical in conventional thermoelectric materials.<sup>44</sup> At a given temperature, the thermopower decreases along with the increase of the magnetization, which indicates a negative magnetothermopower in  $\text{Na}_{0.68}\text{CoO}_2$ , in agreement with the experimental findings.<sup>3</sup> It should be noted that there are no adjustable parameters in our calculations, and the absolute values of the thermopower and its temperature, doping, and magnetization dependence are obtained. We note that experimentally accessible magnetic fields could induce large magnetizations in  $\text{Na}_{0.68}\text{CoO}_2$  at low temperature. In fact, previous LDA calculations suggested strong ferromagnetic (FM) quantum fluctuation in  $\text{Na}_x\text{CoO}_2$ .<sup>45</sup> Experimentally, the low-temperature magnetic susceptibility of  $\text{Na}_{0.67}\text{CoO}_2$  with the magnetic field applied in the  $ab$  plane was found to be rather large.<sup>46</sup> FM in-plane spin fluctuations in  $\text{Na}_{0.75}\text{CoO}_2$  (Ref. 47) and  $\text{Na}_{0.82}\text{CoO}_2$  (Ref. 48) were observed by neutron inelastic scattering. Signatures of induced ferromagnetism were reported in laboratory fields even at lower  $x$  in the charge-ordered regime.<sup>10</sup> Similarly, the misfit compound studied by Limelette *et al.*<sup>6</sup> is near ferromagnetism.<sup>49,50</sup>

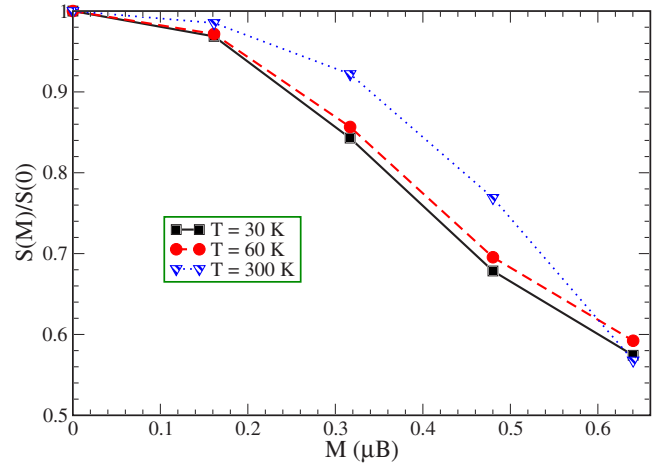


FIG. 3. (Color online) Magnetization dependence of thermopower in  $\text{Na}_{0.68}\text{CoO}_2$  at different temperatures.

To see more clearly the dependence of the thermopower on the magnetization, we calculate the thermopower with different magnetizations at 30, 60, and 300 K. We find that the thermopower can be suppressed by  $\sim 40\%$  in all cases, as shown in Fig. 3. This is in accord with the experimental result,<sup>6</sup> which, however, shows a somewhat larger field suppression. At low temperature, the thermopower increases linearly with the increase of temperature according to the Mott formula.<sup>13</sup> Thus, it is expected that the dependence of the thermopower on the magnetization should be the same at different low temperatures. This is confirmed by our numerical results at 30 and 60 K. Wang *et al.*<sup>3</sup> found that the relationship of the normalized thermopower and magnetization measured at various low  $T$  values collapses to a universal curve. We show that this can be naturally explained using the kinetic transport theory on a high susceptibility material, where magnetization becomes the key parameter.

So far, we have explained the large negative magnetothermopower in  $\text{Na}_{0.68}\text{CoO}_2$  using the Boltzmann transport theory. Here, we turn to the origin of the negative magnetothermopower in this system. Within the two-current model, we can write the total thermopower in another form:

$$S = \frac{L^{11}(\uparrow)S(\uparrow) + L^{11}(\downarrow)S(\downarrow)}{L^{11}(\uparrow) + L^{11}(\downarrow)}, \quad (4)$$

where  $S(\uparrow)$  and  $S(\downarrow)$  are calculated using the spin up and down band structure, respectively. In other words, the total thermopower can be viewed as the average of spin up and down thermopowers weighted by the corresponding conductivity or  $\sigma' = \sigma/\tau$ . Using the NSP band structure of  $\text{Na}_{0.68}\text{CoO}_2$ , we calculate  $S$  and  $\sigma'$  for different doping concentrations within the rigid band approximation. Our result (shown in Fig. 4) indicates that the thermopower in  $\text{Na}_x\text{CoO}_2$  increases along with the increase of  $x$ ,<sup>16</sup> which is consistent with experiment.<sup>4</sup>  $\sigma'$  decreases with increasing  $x$ , as may be expected from the reduction in the number of holes as  $x$  increases. We also did self-consistent calculations at  $x=0.5$ , including the change in O coordinate. This yields a small  $\sim 10\%$  reduction in the calculated thermopower compared to

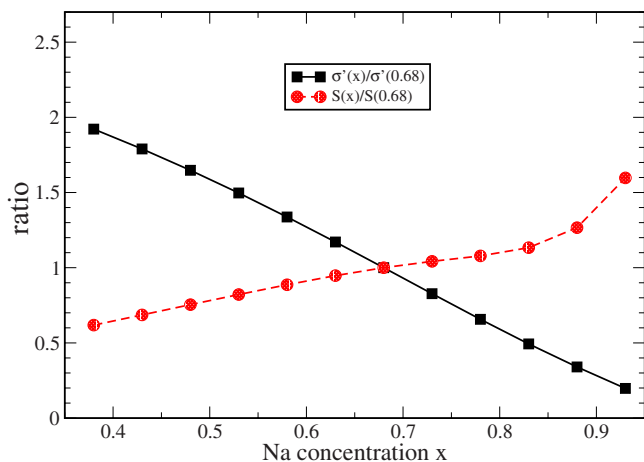


FIG. 4. (Color online) Relative dependence of  $\sigma'$  ( $\sigma' = \sigma/\tau$ ) and  $S$  of  $\text{Na}_x\text{CoO}_2$  on the doping level  $x$ . The 300 K values are used in this plot.

that obtained using the rigid band approximation for  $x=0.5$  applied to the  $x=0.68$  band structure. Similarly, applying the rigid band approximation to the  $x=0.5$  band structure to obtain the thermopower at  $x=0.7$  yields  $\sim 10\%$  lower values than are obtained with the  $x=0.68$  band structure. This reflects the broadening of the bands as  $x$  is reduced.<sup>21</sup> Thus, the slope of the thermopower as a function of  $x$  may be underestimated in the rigid band approximation, but a positive slope is present in both self-consistent virtual crystal and rigid band calculations.

The qualitative dependence of the transport coefficients on  $x$  can be understood as follows: the free-electron conductivity is proportional to the carrier density  $n$ :  $\sigma = \frac{ne^2\tau}{m}$ , where  $m$  is the electron mass, and the carrier density increases along with the decrease of  $x$  due to the increased DOS and hole concentration. Figure 4 shows that the change of  $\sigma'$  is the dominant term. Thus, the total thermopower is mainly from the spin down thermopower, which decreases as more carriers are added to this spin channel, resulting in a negative magnetothermopower.

### III. EFFECT OF SPIN ORBIT

Since the  $t_{2g}$  states are partially occupied in  $\text{Na}_x\text{CoO}_2$ , the spin-orbit coupling (SOC) is not fully quenched, which is responsible for the magnetic anisotropy. In the above calculations, SOC is neglected. Here, we consider the SOC effect

in  $\text{Na}_{0.68}\text{CoO}_2$  using the second-variational method.<sup>51</sup> Since the FSM method cannot be used when SOC is included, we consider two extreme states: the FM and NSP states. For the FM state, we consider two different spin quantization axes: the in-plane  $a$  and out-of-plane  $c$  directions. Our LDA+SOC calculations indicate that  $\text{Na}_{0.68}\text{CoO}_2$  displays an easy-plane anisotropy: the difference between the energy of the in-plane magnetization and that of out-of-plane magnetization is  $-0.20$  meV/Co. The in-plane anisotropy accords with the experimental fact that the in-plane spin susceptibility  $\chi_{ab}$  is larger than  $\chi_c$ .<sup>3,46</sup> Using the band structures from the LDA+SOC calculations, we compute the thermopower using the Boltzmann transport theory. Our result indicates that the effect of SOC on the thermopower in  $\text{Na}_{0.68}\text{CoO}_2$  is small. For the FM case, the room temperature  $S$  values with and without SOC are  $43.4$  and  $44.4$   $\mu\text{V}/\text{K}$ , respectively. The thermopower for the NSP state at 300 K decreases slightly from  $92.3$  to  $89.7$   $\mu\text{V}/\text{K}$  when SOC is taken into account. Thus, our previous results will remain valid with SOC.

### IV. SUMMARY AND CONCLUSIONS

To reiterate, the high thermopower of  $\text{Na}_x\text{CoO}_2$  at metallic carrier densities is due to the narrow manifold of  $t_{2g}$  bands in this material. This narrowness of this manifold can be understood in terms of the bonding topology, in particular, the network of edge sharing  $\text{CoO}_6$  octahedra comprising the  $\text{CoO}_2$  sheets.<sup>24</sup> This topology allows for the coexistence of strong Co-O hybridization and narrow bands. The strong hybridization may weaken the role of Coulomb correlations via screening and may also be responsible for the fact that holes in these sheets are mobile, yielding metallic conduction.

In conclusion, the thermoelectricity in  $\text{Na}_x\text{CoO}_2$  is examined using the standard Boltzmann transport theory combined with spin-polarized density functional theory. The thermopower is found to be smaller when the system is polarized, which thereby provides an alternative explanation for the suppression of thermopower in a magnetic field.

### ACKNOWLEDGMENTS

We are grateful for useful discussions with M.-H. Whangbo. Work at NCSU was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under Grant No. DE-FG02-86ER45259. Research at ORNL was sponsored by DOE, EERE, FreedomCAR, and Vehicle Technologies Program.

\*Corresponding author; singhdj@ornl.gov

<sup>1</sup>G. Mahan, B. Sales, and J. Sharp, Phys. Today **50**(3), 42 (1997).

<sup>2</sup>I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B **56**, R12685 (1997).

<sup>3</sup>Y. Wang, N. S. Rogado, R. J. Cava, and N. P. Ong, Nature (London) **423**, 425 (2003).

<sup>4</sup>M. Lee, L. Viciu, L. Li, Y. Wang, M. L. Foo, S. Watauchi, R. A.

Pascal, Jr., R. J. Cava, and N. P. Ong, Nat. Mater. **5**, 537 (2006).

<sup>5</sup>K. Sakai, M. Karppinen, J. M. Chen, R. S. Liu, S. Sugihara, and H. Yamauchi, Appl. Phys. Lett. **88**, 232102 (2006).

<sup>6</sup>P. Limelette, S. Hébert, V. Hardy, R. Frésard, Ch. Simon, and A. Maignan, Phys. Rev. Lett. **97**, 046601 (2006).

<sup>7</sup>K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature (London) **422**, 53 (2003).

- <sup>8</sup>M. L. Foo, Y. Wang, S. Watauchi, H. W. Zandbergen, T. He, R. J. Cava, and N. P. Ong, *Phys. Rev. Lett.* **92**, 247001 (2004).
- <sup>9</sup>M. Yokoi, T. Moyoshi, Y. Kobayashi, M. Soda, Y. Yasui, M. Sato, and K. Kakurai, *J. Phys. Soc. Jpn.* **74**, 3046 (2005).
- <sup>10</sup>C. H. Wang, X. H. Chen, T. Wu, X. G. Luo, G. Y. Wang, and J. L. Luo, *Phys. Rev. Lett.* **96**, 216401 (2006).
- <sup>11</sup>W. Koshibae, K. Tsutsui, and S. Maekawa, *Phys. Rev. B* **62**, 6869 (2000).
- <sup>12</sup>P. M. Chaikin and G. Beni, *Phys. Rev. B* **13**, 647 (1976).
- <sup>13</sup>W. Jones and N. H. March, *Theoretical Solid State Physics* (Dover, New York, 1985), Vol. 2.
- <sup>14</sup>D. J. Singh, *Phys. Rev. B* **61**, 13397 (2000).
- <sup>15</sup>X. Gao, J. S. Tse, and D. D. Klug, *J. Phys.: Condens. Matter* **16**, 6493 (2004).
- <sup>16</sup>D. J. Singh and D. Kasinathan, *J. Electron. Mater.* **36**, 736 (2007).
- <sup>17</sup>O. I. Motrunich and P. A. Lee, *Phys. Rev. B* **69**, 214516 (2004).
- <sup>18</sup>J. O. Haerter, M. R. Peterson, and B. S. Shastry, *Phys. Rev. Lett.* **97**, 226402 (2006).
- <sup>19</sup>G. Pálsson and G. Kotliar, *Phys. Rev. Lett.* **80**, 4775 (1998).
- <sup>20</sup>T. Takeuchi *et al.*, *Phys. Rev. B* **69**, 125410 (2004).
- <sup>21</sup>M. D. Johannes, D. A. Papaconstantopoulos, D. J. Singh, and M. J. Mehl, *Europhys. Lett.* **68**, 433 (2004).
- <sup>22</sup>See, for example, L. Gravier, A. Fábíán, A. Rudolf, A. Cachin, J.-E. Wegrowe, and J.-Ph. Ansermet, *J. Magn. Magn. Mater.* **271**, 153 (2004).
- <sup>23</sup>L. Chaput, P. Pécheur, and H. Scherrer, *Phys. Rev. B* **75**, 045116 (2007).
- <sup>24</sup>G. B. Wilson-Short, D. J. Singh, M. Fornari, and M. Suewattana, *Phys. Rev. B* **75**, 035121 (2007).
- <sup>25</sup>D. J. Singh and L. Nordstrom, *Planewaves, Pseudopotentials and the LAPW Method*, 2nd ed. (Springer, Berlin, 2006).
- <sup>26</sup>P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, in *WIEN2K, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties*, edited by K. Schwarz (Technische Universität Wien, Wien, Austria, 2001).
- <sup>27</sup>Calculations on other  $\text{Na}_x\text{CoO}_2$  systems indicate similar behavior.
- <sup>28</sup>V. L. Moruzzi, *Phys. Rev. Lett.* **57**, 2211 (1986).
- <sup>29</sup>G. K. H. Madsen and D. J. Singh, *Comput. Phys. Commun.* **175**, 67 (2006).
- <sup>30</sup>M. Z. Hasan *et al.*, *Phys. Rev. Lett.* **92**, 246402 (2004).
- <sup>31</sup>H. B. Yang *et al.*, *Phys. Rev. Lett.* **92**, 246403 (2004).
- <sup>32</sup>H. B. Yang *et al.*, *Phys. Rev. Lett.* **95**, 146401 (2005).
- <sup>33</sup>D. Qian *et al.*, *Phys. Rev. Lett.* **96**, 046407 (2006).
- <sup>34</sup>M. Z. Hasan, D. Qian, Y. Li, A. V. Fedorov, Y. D. Chuang, A. P. Kuprin, M. L. Foo, and R. J. Cava, arXiv:cond-mat/0501530 (unpublished); M. Z. Hasan, D. Qian, M. L. Foo, and R. J. Cava, *Ann. Phys.* **321**, 1568 (2006).
- <sup>35</sup>P. Zhang, W. Luo, M. L. Cohen, and S. G. Louie, *Phys. Rev. Lett.* **93**, 236402 (2004).
- <sup>36</sup>K. W. Lee, J. Kunes, and W. E. Pickett, *Phys. Rev. B* **70**, 045104 (2004).
- <sup>37</sup>A. G. Petukhov, I. I. Mazin, L. Chioncel, and A. I. Lichtenstein, *Phys. Rev. B* **67**, 153106 (2003).
- <sup>38</sup>G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet, and C. A. Marianetti, *Rev. Mod. Phys.* **78**, 865 (2006).
- <sup>39</sup>N. L. Wang, P. Zheng, D. Wu, Y. C. Ma, T. Xiang, R. Y. Jin, and D. Mandrus, *Phys. Rev. Lett.* **93**, 237007 (2004).
- <sup>40</sup>M. D. Johannes, I. I. Mazin, and D. J. Singh, *Phys. Rev. B* **71**, 205103 (2005).
- <sup>41</sup>H. Ishida, M. D. Johannes, and A. Liebsch, *Phys. Rev. Lett.* **94**, 196401 (2005).
- <sup>42</sup>C. A. Perroni, H. Ishida, and A. Liebsch, *Phys. Rev. B* **75**, 045125 (2007).
- <sup>43</sup>D. J. Singh and D. Kasinathan, *Phys. Rev. Lett.* **97**, 016404 (2006).
- <sup>44</sup>D. J. Singh, *Semiconductors and Semimetals* (Academic, New York, 2000), Vol. 70, p. 125.
- <sup>45</sup>D. J. Singh, *Phys. Rev. B* **68**, 020503(R) (2003).
- <sup>46</sup>F. C. Chou, J. H. Cho, and Y. S. Lee, *Phys. Rev. B* **70**, 144526 (2004).
- <sup>47</sup>A. T. Boothroyd, R. Coldea, D. A. Tennant, D. Prabhakaran, L. M. Helme, and C. D. Frost, *Phys. Rev. Lett.* **92**, 197201 (2004).
- <sup>48</sup>S. P. Bayrakci, I. Mirebeau, P. Bourges, Y. Sidis, M. Enderle, J. Mesot, D. P. Chen, C. T. Lin, and B. Keimer, *Phys. Rev. Lett.* **94**, 157205 (2005).
- <sup>49</sup>I. Tsukada, T. Yamamoto, M. Takagi, T. Tsubone, S. Konno, and K. Uchinokura, *J. Phys. Soc. Jpn.* **70**, 834 (2001).
- <sup>50</sup>A. Maignan, S. Hébert, M. Hervieu, C. Michel, D. Pelloquin, and D. Khomskii, *J. Phys.: Condens. Matter* **15**, 2711 (2003).
- <sup>51</sup>J. Kuneš, P. Novák, M. Diviš, and P. M. Oppeneer, *Phys. Rev. B* **63**, 205111 (2001), and references therein.