Effect of partial La filling on the local electronic properties of La$_x$Co$_4$Sb$_{12}$ studied using $^{59}$Co NMR

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Abstract. We present a systematic investigation of the La$_x$Co$_4$Sb$_{12}$ skutterudites with $x \leq 0.2$ using $^{59}$Co nuclear magnetic resonance (NMR) spectroscopy. The NMR line shape, the quadrupole splitting, the Knight shift and the spin–lattice relation rate of each compound have been identified. For La$_x$Co$_4$Sb$_{12}$, the central transition and the quadrupole linewidths increase with the La concentration because of the effect of the inhomogeneous electric field gradient. In addition, each linewidth exhibits a temperature-independent behavior, confirming the non-magnetic characteristic of these materials. The results of the isotropic Knight shift and the spin-lattice relaxation rate provide further information on the electronic structure around the Fermi surfaces of these compounds. In La$_{0.1}$Co$_4$Sb$_{12}$ and La$_{0.2}$Co$_4$Sb$_{12}$, the low-temperature NMR relaxation rates follow the Korringa behavior, indicating a finite density of carriers at the Fermi level. The high-temperature relaxation rates go over to a semiconductor-like activated form, being consistent with a semimetallic response. A detailed analysis of the spin-lattice relaxation rate established that the partial Co 3d Fermi-level density of states (DOS) increases with the La content. The NMR observations were interpreted in terms of a two-band scenario that consists of predominant d-electron features at low temperatures and exotic behavior of s-character electrons at high temperatures. Moreover, the obtained Fermi-level DOS show good agreement with those observed from the electrical conductivity and the Seebeck coefficient measurements in these La-filled skutterudites.

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1. Introduction

There has been considerable interest in the skutterudite compound CoSb$_3$ because of its unusual electronic properties and promising potential for thermoelectric applications [1]. This compound crystallizes in the cubic space group of $Im\bar{3}$ (figure 1). The unit cell contains eight small cubes and a large void appears within each of the two cubes. These voids can be filled by various elements such as Ca, Sr, La and Ce so as to form the so-called filled skutterudites M$_x$Co$_4$Sb$_{12}$ (where M is the filler atom and x is the partial filling fraction) [2]. In M$_x$Co$_4$Sb$_{12}$, the lattice thermal conductivity ($\kappa_L$) could be significantly reduced because of the scattering of the thermal phonons by the rattling of the filler atoms [3]–[10]. This reduced $\kappa_L$ readily leads to improvement of the thermoelectric performance according to the thermoelectric figure of merit $Z = S^2\sigma/\kappa$, where $S$, $\sigma$ and $\kappa$ are the Seebeck coefficient, electrical conductivity and total thermal conductivity, respectively. In addition, the filling of proper atoms could result in the enhancements of $S$ and/or $\sigma$, and such enhancements can be ascribed to an electronic origin, especially the change of electronic features in the vicinity of the Fermi surfaces.

A large number of theoretical calculations have been performed to understand the band structures in M$_x$Co$_4$Sb$_{12}$ with the main focus being on the correlation with the measured transport properties [11]–[15]. In Ca$_x$Co$_4$Sb$_{12}$ for example, an increase in the Ca concentration is accompanied by increased Fermi-level density of states (DOS), $N(E_F)$, and an otherwise minor change in the band structures [15]. Such a result seems to imply that a band-filling picture would be suitable for explaining the sign and trend of the Seebeck coefficients [16], because the filling of the divalent Ca ions has the same effect as doping electrons to CoSb$_3$ [17]. Although there are many theoretical reports related to this band-filling scenario [11]–[15], there has been little associated experimental work, which is, however, essential for providing a microscopic insight into the band structure variation as filling atoms are added in the voids of CoSb$_3$.

Nuclear magnetic resonance (NMR) measurement is known as an atomic probe in metallic alloys, yielding information on the Fermi surface features [18]. In the present study, we employed NMR techniques to study the electronic characteristics of La$_x$Co$_4$Sb$_{12}$ in order to understand how the electronic nature varies upon La filling. Experimental NMR results including the powder patterns, the Knight shifts and the spin-lattice relaxation rates of $x = 0.1$ and 0.2 in La$_x$Co$_4$Sb$_{12}$ have been presented. We have also included the previous measurements...
Figure 1. Crystal structure of CoSb$_3$.

of CoSb$_3$ for comparison. The NMR observations were correlated with the local electronic properties of La$_x$Co$_4$Sb$_{12}$ using a simple two-band model.

### 2. Experimental details

Polycrystalline La$_x$Co$_4$Sb$_{12}$ samples were prepared from 99.9% La, 99.95% Co and 99.999% Sb by mixing appropriate amounts of these elemental metals, followed by melting in an induction furnace under partial argon. Because of the volatility of Sb at high temperatures, a 3 mol% excess of Sb from the stoichiometry was adopted. To further promote homogeneity, the resulting ingots were annealed in a vacuum-sealed quartz tube at 800°C for 3 days followed by furnace cooling. For each specimen, x-ray powder diffraction was performed (Cu K$_\alpha$1 radiation; Bruker D8 Advance). As shown in figure 2(a), the associated Rietveld analysis using the General Structure Analysis System (GASA) program revealed the phase purity, homogeneity and stoichiometry attained (see also table 1). In $x = 0.1$, a weak impurity peak appears (denoted by an asterisk in figure 2(a)), while it has little effect on the NMR measurements. In $x = 0.1$ and 0.2, the exceptionally large atomic displacement parameters (ADPs) of La compared with those of Co and Sb were suggested to be a characteristic of the rattling of the filler atoms at this rattler site [3]–[10]. Our attempts to reduce these ADPs by displacing La to the other crystallographic sites with a lower site symmetry resulted in otherwise unstable refinements, confirming the rattling nature of La (large ADPs) at this site. The decrease in ADPs with increasing La content (see table 1), however, indicates that the reduction of the rattling is probably due to a decrease in the spatial degree of freedom for the surrounding local environment.

The variation of the lattice constant as a function of the La concentration is plotted in figure 2(b). It is clear that the lattice parameter increases with the La concentration, indicating that the voids of CoSb$_3$ are successfully filled by La in accordance with Vegard’s law. It is worth mentioning that a sample with the nominal composition of $x = 0.3$ was also fabricated under the same preparation conditions. Although the observed x-ray powder diffraction pattern
Figure 2. (a) The Rietveld refinements of the x-ray powder diffraction patterns of La$_x$Co$_4$Sb$_{12}$ with $x = 0.1$ and 0.2. The asterisk in $x = 0.1$ indicates a weak unidentified impurity peak. (b) Lattice constant and quadrupole frequency $\nu_Q$ as a function of the La concentration $x$. Note that $\nu_Q$ is shown by a negative direction. The corresponding solid and dashed lines are a guide to the eye for the linear tendency.
Table 1. The Rietveld refined atomic positions (x, y, z), site occupancies (n) and ADPs (U$_{iso}$) of La$_{0.1}$Co$_4$Sb$_{12}$ and La$_{0.2}$Co$_4$Sb$_{12}$ at room temperature in the space group Im$\bar{3}$.

| Atom | Site | x   | y$^1$ | z   | n   | U$_{iso}$ |
|------|------|-----|------|-----|-----|----------|
| La   | 2a   | 0   | 0    | 0   | 0.1 | 0.094(23) |
|      |      |     |      |     | 0.2 | 0.067(11) |
| Co   | 8c   | 1/4 | 1/4  | 1/4 | 1   | 0.017(10) |
|      |      |     |      |     | 1   | 0.011(9)  |
| Sb   | 24g  | 0   | 0.3341(1) | 0.1570(1) | 1 | 0.013(2) |
|      |      |     | 0.3349(1) | 0.1580(1) | 1 | 0.016(2) |

$^1$For each tabulated refined result, the first row is for La$_{0.1}$Co$_4$Sb$_{12}$ and the second row is for La$_{0.2}$Co$_4$Sb$_{12}$. The refined lattice constants of La$_{0.1}$Co$_4$Sb$_{12}$ and La$_{0.2}$Co$_4$Sb$_{12}$ are 9.042 04(3) Å and 9.050 86(3) Å, respectively. For La$_{0.1}$Co$_4$Sb$_{12}$ (La$_{0.2}$Co$_4$Sb$_{12}$), the refined R factors and $\chi^2$ goodness of fit are $R_p = 7.52\%$ (6.71%), $R_{wp} = 9.48\%$ (8.47%) and $\chi^2 = 2.568(1.895)$. All site occupancies have been refined, while they exhibited negligible deviations from the nominal compositions. The site occupancies were thus kept as the nominal values throughout the refinements.

exhibits a single-phase feature, the corresponding lattice constant deviates from the expected linear dependence, suggesting that this filling level could be beyond the solubility limit for La in CoSb$_3$. As a matter of fact, several theoretical calculations have predicted that $x \approx 0.2$ is the filling limit in La$_x$Co$_4$Sb$_{12}$ [19, 20].

NMR experiments were performed using a Varian 300 spectrometer, with a home-built probe employed for both room-temperature and low-temperature measurements. Each powdered specimen was put in a plastic vial that showed no observable $^{59}$Co NMR signal. The Knight shift in La$_x$Co$_4$Sb$_{12}$ was referred to the $^{59}$Co resonance frequency of one molar of aqueous K$_3$Co(CN)$_6$ at 71.386 MHz. This reference frequency gives rise to the $^{59}$Co nuclear gyromagnetic ratio ($\gamma_n$) of $2 \pi \times 1.0102 \times 10^3$ Hz $\text{G}^{-1}$ upon the application of a constant field, 7.0665 T.

2.1. Powder pattern

Because of the electric quadrupole coupling, the $^{59}$Co NMR spectrum ($I = \frac{7}{2}$) consists of six satellite lines, as illustrated in figure 3. The wide-line satellite spectra were mapped out by integrating the spin echo signal of various excitations. Since the cubic I$\bar{m}3$ structure contains a single Co site and is axially symmetric, it appears as a one-site NMR spectrum for each of the studied compositions. For the powder specimens, as in our experiment, these lines exhibit a typical powder pattern, with the distinctive edges corresponding to the quadrupole parameter. Since the first-order quadrupole interaction is the main effect shaping these lines, the quadrupole frequency, $\nu_Q$, was estimated directly from these lines. The determined $\nu_Q$ values are summarized in table 2.

It is clear that $\nu_Q$ gradually decreases with increasing $x$ for La$_x$Co$_4$Sb$_{12}$, suggesting a reduction of the local electric field gradient (EFG) via the La filling. The decrease in EFG is related to the longer Co–Co distance arising from the lattice expansion (Co–Co length; half
Figure 3. Resolved $^{59}$Co NMR satellite lines for La$_x$Co$_4$Sb$_{12}$.

| $x$ | $\nu_Q$ (MHz) | $K_o$ (%) | $A_1$ ($10^{-5}$ K$^{-1/2}$) | $A_2$ ($10^{-5}$ s$^{-1}$K$^{-2}$) | $1/T_{1K}$ (s$^{-1}$ K$^{-1}$) | $N_d(E_F)$ |
|-----|--------------|----------|------------------------------|-----------------|-------------------|-----------|
| 0   | 1.18         | -0.042   | 3.17                         |                 |                   |           |
| 0.1 | 1.06         | -0.098   | 158                          | 133             | 0.194             | 0.794     |
| 0.2 | 0.94         | -0.148   | 260                          | 370             | 0.218             | 0.844     |

of the lattice constant). In figure 2(b) $\nu_Q$ is plotted as a function of the La concentration for a direct comparison with the variation of the lattice constant. Indeed both quantities correlate with each other nicely, supporting the proposed argument.

It is apparent that the sharp satellite line edge gradually smears out with increasing La filling content in the voids of CoSb$_3$, and this feature is mainly due to the randomness of the local EFG that has been known to broaden the satellite line effectively. One may speculate that the observed line broadening could be related to the rattling of La, which is expected to reduce with decreasing temperature [21]. The NMR linewidths for all studied compositions are, however, almost temperature-independent, indicating that the rattling has a negligible effect on the line broadening.

Figure 4 shows the room-temperature central transition line ($m = \frac{1}{2} \leftrightarrow -\frac{1}{2}$) for La$_x$Co$_4$Sb$_{12}$, obtained from the fast Fourier transform of the spin echo using a standard $\pi/2$ – $\tau$ – $\pi$ sequence. The observed spectrum splits into two peaks because of the simultaneous presence of the anisotropic Knight shift and the second-order quadrupole interactions. It is important to note that the feature of the line shapes remains unchanged with decreasing
Figure 4. $^{59}$Co NMR central transition spectra for La$_x$Co$_4$Sb$_{12}$ measured at room temperature. Simulated powder patterns for $x = 0.1$ and 0.2, drawn as dotted curves, have been shifted down for clarity. Each arrow indicates the frequency for the isotropic Knight shift.

Temperature, indicative of the non-magnetic nature of La$_x$Co$_4$Sb$_{12}$. This characteristic confirms that the filling of La in the voids of CoSb$_3$ does not induce noticeable magnetic moments on the Co sites. Similar to the satellite lines, the central transition linewidth gradually broadens with adding more La content. This could be ascribed to an increase in the degree of the hyperfine field inhomogeneity. We performed a shape function fitting with a proper broadening factor to reproduce the synthetic spectrum for each individual composition. For a polycrystalline sample, the shape function fitting for the combination of the quadrupole and the anisotropic Knight shift interactions was first presented by Jones et al [22]. Because of the cubic structure of La$_x$Co$_4$Sb$_{12}$, the $^{59}$Co quadrupole shift and the angle-dependent Knight shift are axially symmetric. Therefore, the frequency shift of the central transition, $\Delta \nu$, can be written as

$$\frac{\Delta \nu}{\nu_o} = \frac{2K_{an}}{1 + K_{iso}} (3 \cos^2 \theta - 1) + \frac{15}{16} \left( \frac{\nu_Q}{\nu_o} \right)^2 (1 - \cos^2 \theta)(1 - 9 \cos^2 \theta).$$

(1)

Here, $\nu_o$ is the Larmor frequency, $K_{iso}$ the isotropic Knight shift, $K_{an}$ the anisotropic Knight shift and $\theta$ the angle between the crystal symmetry axis and the external magnetic field. The central transition line simulation appropriate to each powder sample was performed according to equation (1). By substituting $\nu_Q$ and tuning $K_{an}$, the synthetic profile was thus obtained and matches well with the experimental $^{59}$Co NMR spectra. For each material, the best-fit result, shown as a dotted curve in figure 4, yields the corresponding $K_{iso}$ and $K_{an}$ values.

2.2. Knight shift

Figure 5 shows the temperature dependence of the $^{59}$Co NMR isotropic Knight shift for La$_x$Co$_4$Sb$_{12}$. The observation is a combination of two terms: $K_{iso}(T) = K_o + K(T)$. The $K_o$ term represents the $T$-independent shift, and $K(T)$ dictates the shift to higher frequencies.
Figure 5. Temperature dependence of $^{59}$Co isotropic Knight shifts for $La_xCo_4Sb_{12}$. Dotted curves: fit to the semimetallic behavior from equation (2).

with increasing temperature. The exotic behavior can be easily understood as the increase in the number of carriers arising from the thermal excitation across an energy gap, $\Delta$. Under an effective mass approximation for the band edges with the Fermi energy located at the midgap, the isotropic Knight shift can be written as

$$K_{iso} = K_0 + A_1 \sqrt{T} e^{-\Delta/2k_B T},$$

(2)

where $A_1 = \frac{2}{3\sqrt{\hbar}} (2\pi)^{3/2} \gamma_e^2 \langle |u_k(0)|^2 \rangle_{EF} (m^*_e)^{3/2} (m^*_h)^{3/4} \sqrt{k_B}$ is associated with the effective masses of electron and hole carriers denoted by $m^*_e$ and $m^*_h$, respectively. In the expression of $A_1$, $\hbar$, $\gamma_e$ and $k_B$ represent the reduced Planck constant, the electronic gyromagnetic ratio and the Boltzmann constant, respectively. $\langle |u_k(0)|^2 \rangle_{EF}$ represents the square of the wavefunction at the nucleus averaged over those electrons with the average wave vector $k$ at the Fermi surface. Here, each carrier density varies with temperature in accordance with the relation $T^{3/2} \exp(-\Delta/2k_B T)$. On the basis of the band structure calculations, the filling of La in the voids of CoSb$_3$ shows negligible effects on the modification of the gap size [24]. For each fit, we thus fixed the energy gap of $\Delta/k_B = 460$ K, which was reported for CoSb$_3$ [25]. The fitting, shown as solid curves in figure 5, gives rise to $K_0$ and $A_1$, and these results are summarized in table 2.

It is clear that the sign of $K_0$ is negative for all studied materials and the corresponding absolute value increases with the La concentration. For the semiconducting CoSb$_3$ compound, $K_0$ has been interpreted as a diamagnetic shift [25]. For $La_{0.1}Co_4Sb_{12}$ and $La_{0.2}Co_4Sb_{12}$, $K_0$ is a combination of the Fermi contact, the orbital and the d-spin shifts. Note that the d-spin shift is negative because of the negative d-electron hyperfine coupling for the core-polarization mechanism [24], and this term is proportional to the partial Co 3d Fermi-level DOS, $N_d(E_F)$. The negative value of $K_0$ for these La-filled skutterudites thus suggests that the d-spin shift is a
dominant term for the observed $T$-independent shift. Moreover, the magnitude of $K_0$ becomes larger with increasing $x$ in La$_x$Co$_4$Sb$_{12}$, indicative of an increase in $N_d(E_F)$ with adding more La content in the voids of CoSb$_4$.

On the other hand, the $T$-dependent part reflects an increase in the spin susceptibility, which is attributed to an increase in the density of carriers through the thermal activation and is also responsible for the enhancement of the relaxation rate. It thus seems reasonable to suggest that the thermally excited spin susceptibility could be strongly correlated with the d-electrons considering the narrow d bands in La$_x$Co$_4$Sb$_{12}$. However, such an argument is unlikely because the negative core polarization induced by the spin susceptibility of the Co d states will shift the resonance peak to lower frequencies with increasing temperature. Therefore, we can conclude that the thermally excited carriers in La$_{0.1}$Co$_4$Sb$_{12}$ and La$_{0.2}$Co$_4$Sb$_{12}$ are mainly s-like with the positive s-hyperfine constant being responsible for the $T$-dependent Knight shifts and spin-lattice relaxation rates at higher temperatures. It is interesting that the prefactor $A_1$ increases with the La content, also consistent with the characteristics for $A_2$. This feature implies that the ratio $m_s^x/m_s^z$ gradually increases with insertion of La in the voids of CoSb$_4$.

2.3. Spin-lattice relaxation rate

The temperature dependence of the spin-lattice relaxation rate ($1/T_1$) was measured using the inversion recovery method. The signal strength was acquired by integrating the recovered spin echo signal. In this experiment, the relaxation process involves the adjacent pairs of spin levels, and the corresponding spin-lattice relaxation is a multiexponential expression [26]. For the central transition with $I = 7/2$, the recovery of the nuclear magnetization can be expressed as

$$\frac{M(t) - M(\infty)}{M(\infty)} = -2\alpha(0.012 e^{-t/T_1} + 0.068 e^{-6t/T_1} + 0.206 e^{-15t/T_1} + 0.714 e^{-28t/T_1}).$$

(3)

Here, $\alpha$ is a fractional value derived from the initial conditions used in our experiments. $M(t)$ is the nuclear magnetization at the recovery time $t$ and $M(\infty)$ represents the magnetization after the long-time recovery. Each experimental $T_1$ value was obtained by such a fitting to the multiexponential recovery curve. Figure 6 depicts the temperature dependence of $1/T_1$ for La$_x$Co$_4$Sb$_{12}$, and we have included the previous data on CoSb$_3$ for comparison [25].

Upon raising the temperature, $1/T_1$ for La$_{0.1}$Co$_4$Sb$_{12}$ and La$_{0.2}$Co$_4$Sb$_{12}$ rises rapidly, suggesting a temperature-activated dependence. This is a characteristic response for semiconductors arising from an increase of thermally excited carriers. It is, therefore, reasonable to reconcile the metallic behavior observed at low temperatures with the high-$T$ semiconducting feature using a two-band model, with one band overlapping the Fermi level, while the other band is separated from the Fermi level by an energy gap. By analogy to the Knight shift, the relaxation rate is given by [23]

$$\frac{1}{T_1 T} = \frac{1}{T_{1K} T} + A_2 T e^{-\Delta/2k_B T}.$$  \hspace{1cm} (4)

Here, $1/T_{1K} T$ is the inverse Korringa constant and is generally related to the partial Fermi-level DOS of the probed site. The second term represents the band edge separated from the Fermi level, associated with a constant $A_2$. Here, $A_2 = \frac{128}{\pi^2 \hbar^3} \left(\frac{E_F}{\beta T}\right)^2 \left(\frac{\beta T}{m_T^z}\right)^3 \left(\frac{m_T^z}{m_T^x}\right)^{3/2} k_B^2$ depends on the same factors as $A_1$. We thus fit the observed $1/T_1 T$ data on La$_{0.1}$Co$_4$Sb$_{12}$ and La$_{0.2}$Co$_4$Sb$_{12}$ to equation (4) with $1/T_{1K} T$ and $A_2$ as parameters. It is remarkable that these fits are quite
Figure 6. Temperature variation of $^{59}\text{Co}$ spin-lattice relaxation rates for $\text{La}_x\text{Co}_4\text{Sb}_{12}$. Dotted curves: fit to the semimetallic character from equation (4) for $\text{La}_{0.1}\text{Co}_4\text{Sb}_{12}$ and $\text{La}_{0.2}\text{Co}_4\text{Sb}_{12}$. Note that the magnitude of the relaxation rates for $\text{CoSb}_3$ has been multiplied by a factor of 100 for clarity.

satisfactory over the entire temperature range, shown as dotted curves in figure 6. The values of $1/T_{1K}T$ and $A_2$ were thus extracted from these fits and the results are summarized in table 2.

3. Discussion

Recent theoretical calculations on $\text{La}_x\text{Co}_4\text{Sb}_{12}$ indicated that the Co 3d bands are all at the Fermi level with a few s-character electrons near the Fermi surface [27]. The Korringa relaxation process for $\text{La}_x\text{Co}_4\text{Sb}_{12}$ is thus dominated by the d-spin relaxation rate and can be expressed as

$$\frac{1}{T_{1K}T} = 2\hbar k_B [\gamma_n H_{hf}^d N_d(E_F)]^2 q.$$  (5)

Here, $\gamma_n$ is the $^{59}\text{Co}$ nuclear gyromagnetic ratio and $N_d(E_F)$ is the Co 3d Fermi-level DOS in units of states per eV spin. The variable $H_{hf}^d$ represents the core-polarization hyperfine field per electron, taken to be $-1.8 \times 10^5$ gauss for the cobalt-based metals [28]. The constant $q$ is a reduction factor equal to the reciprocal of the degeneracy. For the electron pockets located at $\Gamma$, as revealed from the band structure calculations [27], the cobalt d-electron manifold shows a 3-fold degeneracy, giving $q = 1/3$. Using these parameters and experimental $(1/T_{1K}T)$ values, we then obtained $N_d(E_F)$ for each composition of $\text{La}_x\text{Co}_4\text{Sb}_{12}$, and the results are tabulated in table 2. Indeed, the value of $N_d(E_F)$ gradually increases with subscript $x$ in $\text{La}_x\text{Co}_4\text{Sb}_{12}$, consistent with the observation on the Knight shift.

On the other hand, the activated relaxation is characterized by the response to the thermally excited s-character electrons across the band edges. Such an interpretation is in agreement with the semimetallic characteristic of $\text{La}_{0.1}\text{Co}_4\text{Sb}_{12}$ and $\text{La}_{0.2}\text{Co}_4\text{Sb}_{12}$, as described in the isotropic

New Journal of Physics 10 (2008) 083029 (http://www.njp.org/)
Knight shift. According to equation (4), this relaxation process is related to the constant $A_2$, with which the ratio of $m_h^*/m_e^*$ is associated. It should be noted that the determined $A_2$ values for $\text{La}_{0.1}\text{Co}_4\text{Sb}_{12}$ and $\text{La}_{0.2}\text{Co}_4\text{Sb}_{12}$ are about two orders of magnitude larger than that for CoSb$_3$, indicating that the effective hole mass turns out to be heavier after the filling of La atoms in the voids of CoSb$_3$. As a consequence, the lighter n-type carriers dominate the transport properties, leading to negative Seebeck coefficients in these La-filled skutterudites [29].

Most importantly, the present NMR observations can be interpreted well in terms of a simple two-band model with the low-temperature features dominated by the d-electrons and the high-temperature exotic behavior dictated by the s-character electrons. The change in the d-electron DOS at the Fermi level was found to be in good agreement with the variations in the electrical conductivity and the Seebeck coefficient [29]. The observed enhancement of the electrical conductivity with increasing $x$ for $\text{La}_x\text{Co}_4\text{Sb}_{12}$ can easily be accounted for by the increase in $N_d(E_F)$. For the Seebeck coefficient, the diffusion thermoelectric power in transition metals can approximately be written as [30].

$$S(T) = -\frac{\pi^2 k_B^2 T}{3e} \left[ \frac{1}{N(E)} \frac{\partial N(E)}{\partial E} \right]_{E=E_F}$$ (6)

It is generally true that a high Seebeck coefficient is brought about by a low $N(E_F)$ combined with its steep slope, $\partial N(E)/\partial E$, in the vicinity of $E_F$. The fact that $S$ in $\text{La}_{0.23}\text{Co}_4\text{Sb}_{12}$ at room temperature ($S \approx -80 \mu V K^{-1}$) is lower than that in $\text{La}_{0.05}\text{Co}_4\text{Sb}_{12}$ ($S \approx -160 \mu V K^{-1}$) can be connected to a higher $N(E_F)$ value in the former compound [29]. Therefore, agreement is obtained for the deduced $N_d(E_F)$ probed by $1/T_1 T$ as compared with the variation of the Seebeck coefficient in $\text{La}_x\text{Co}_4\text{Sb}_{12}$.

4. Conclusions

NMR measurements have provided a local picture of the electronic properties of $\text{La}_x\text{Co}_4\text{Sb}_{12}$ with $x \leq 0.2$. The observed $T$-dependent isotropic Knight shifts and the spin-lattice relaxation rates are understood in the framework of the semimetallic characteristics, with a small band overlap at the Fermi level falling within a pseudogap formed by nearby bands. The changes in the electronic features revealed by the NMR relaxation rates can easily be explained by a simple two-band scenario that is consistent with those calculated from the band-structure methods. Furthermore, the variation of the Fermi-level DOS was found to be in agreement with those observed from the electrical conductivity and the Seebeck coefficient measurements in these La-filled skutterudites.

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