75As NMR Studies of Magnetic Properties of the Magnetic Superconductor CaK(Fe0.967Ni0.033)4As4

Qing-Ping Ding  
_Iowa State University and Ames Laboratory, qpding@ameslab.gov_

William R. Meier  
_Iowa State University and Ames Laboratory, wmeier@iastate.edu_

Anna E. Böhmer  
_Iowa State University and Ames Laboratory_

Sergey L. Bud’ko  
_Iowa State University and Ames Laboratory, budko@ameslab.gov_

Paul C. Canfield  
_Iowa State University and Ames Laboratory, canfield@ameslab.gov_

_See next page for additional authors_

Follow this and additional works at: https://lib.dr.iastate.edu/ameslab_manuscripts

Part of the _Physics Commons_

_Recommended Citation_

Ding, Qing-Ping; Meier, William R.; Böhmer, Anna E.; Bud’ko, Sergey L.; Canfield, Paul C.; and Furukawa, Yuji, "75As NMR Studies of Magnetic Properties of the Magnetic Superconductor CaK(Fe0.967Ni0.033)4As4" (2019). _Ames Laboratory Accepted Manuscripts_. 480.  
https://lib.dr.iastate.edu/ameslab_manuscripts/480

This Article is brought to you for free and open access by the Ames Laboratory at Iowa State University Digital Repository. It has been accepted for inclusion in Ames Laboratory Accepted Manuscripts by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
75As NMR Studies of Magnetic Properties of the Magnetic Superconductor CaK(Fe0.967Ni0.033)4As4

Abstract
We have carried out 75As nuclear magnetic resonance (NMR) measurements to investigate a new antiferromagnetic (AFM) state, the so-called hedgehog spin-vortex crystal (SVC) in CaK(Fe0.967Ni0.033)4As4. The hedgehog SVC order is clearly demonstrated by the direct observation of internal magnetic induction along the c axis at the As1 site (close to K) and a zero net internal magnetic induction at the As2 site (close to Ca) below an AFM ordering temperature of TN \sim 45 \text{ K}. In the superconducting (SC) state, the NMR signal intensity decreases suddenly just below T_c \sim 20 \text{ K} due to Meissner effect, evidencing the coexistence of the hedgehog SVC AFM and SC states from a microscopic point of view.

Keywords
Iron based superconductor, nuclear magnetic resonance, spin-vortex crystal antiferromagnetic state

Disciplines
Physics

Authors
Qing-Ping Ding, William R. Meier, Anna E. Bömmer, Sergey L. Bud’ko, Paul C. Canfield, and Yuji Furukawa

This article is available at Iowa State University Digital Repository: https://lib.dr.iastate.edu/ameslab_manuscripts/480
As NMR studies of magnetic properties of the magnetic superconductor CaK(Fe$_{0.967}$Ni$_{0.033}$)$_4$As$_4$

Qing-Ping Ding$^1$, William R. Meier$^{1,8}$, Anna E. Böhmer$^{1,9,†}$, Sergey L. Bud’ko$^{1,5}$, Paul C. Canfield$^{1,5}$, and Yuji Furukawa$^{1,5}$

$^1$Ames Laboratory, U.S. DOE, Ames, and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA

$^8$qingping.ding@gmail.com, $^5$wmeier@iastate.edu, $^9$anna.boehmer@kit.edu, $^5$budko@ameslab.gov, $^6$canfield@ameslab.gov, $^1$furukawa@ameslab.gov

Keywords: Iron based superconductor, nuclear magnetic resonance, spin-vortex crystal antiferromagnetic state.

We have carried out $^{75}$As nuclear magnetic resonance (NMR) measurements to investigate a new antiferromagnetic (AFM) state, the so-called hedgehog spin-vortex crystal (SVC) in CaK(Fe$_{0.967}$Ni$_{0.033}$)$_4$As$_4$. The hedgehog SVC order is clearly demonstrated by the direct observation of internal magnetic induction along the $c$ axis at the As1 site (close to K) and a zero net internal magnetic induction at the As2 site (close to Ca) below an AFM ordering temperature of $T_N \sim 45$ K. In the superconducting (SC) state, the NMR signal intensity decreases suddenly just below $T_c \sim 20$ K due to Meissner effect, evidencing the coexistence of the hedgehog SVC AFM and SC states from a microscopic point of view.

Introduction

Recently much attention has been paid to the magnetic properties of Fe-based superconductors (SCs). In most of Fe based SCs such as the so-called 122-type family AFe$_2$As$_2$ ($A = $ Ca, Ba, Sr, Eu), by lowering the temperature, the crystal structure changes from high-temperature tetragonal to low-temperature orthorhombic at, or just above, a system-dependent Neel temperature $T_N$, below which long-range stripe-type antiferromagnetic (AFM) order emerges [1-3].

The magnetism in the Fe-based SCs can be characterized by the spatial variation of the iron magnetic moment at a position $r$, $S(r) = M_1 \exp[iQ_1 \cdot r] + M_2 \exp[iQ_2 \cdot r]$, where $Q_1 = (\pi,0)$ and $Q_2 = (0,\pi)$ are wave vectors (using the single-iron Brillouin zone notation) [4-7]. $M_1$ and $M_2$ are the magnetic order parameters associated with the two wave vectors $Q_1$ and $Q_2$, respectively. The stripe-type antiferromagnetic state in orthorhombic structure phase can be described by taking only one nonzero $M_i$, which is called single-$Q$ state. The schematic view of the stripe-type antiferromagnetic spin structure is shown in Fig. 1(b).

When both $M_1$ and $M_2$ are finite (called double-$Q$ state), other interesting magnetic states can appear. In the case that $M_1$ and $M_2$ are either parallel or antiparallel, a nonuniform magnetic state is produced where the average moment at one lattice site vanishes and a staggered-like order appears at the other lattice sites as shown in Fig. 1(c) [6]. This so-called spin-charge density wave (SCDW) has been realized in Sr$_{1-x}$Na$_x$Fe$_2$As$_2$ [8], and likely occurs in Ba(Fe$_{1-x}$Mn$_x$)$_2$As$_2$, Ba$_{1-x}$Na$_x$Fe$_2$As$_2$, and Ba$_{1-x}$K$_x$Fe$_2$As$_2$ as well [9-15]. A possible coexistence of SCDW and superconductivity is reported in Ba$_{1-x}$Na$_x$Fe$_2$As$_2$ [10], and Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [10,13,15]. When $M_1$ and $M_2$ are orthogonal and $|M_1| = |M_2|$, the two different double-$Q$ magnetic structures are possible. Depending on the relative angle between $Q_i$ and $M_i$ vectors, so-called loop-type spin vortex crystal (SVC) state for $M_i \perp Q_i$, and hedgehog-type SVC state for $M_i \parallel Q_i$ (see, Fig. 1(d) and 1(e)) have been predicted theoretically [6].

Recently, the hedgehog SVC antiferromagnetic state with tetragonal symmetry has been actually discovered in the electron-doped 1144-type iron pnictide SCs CaK(Fe$_{1-x}$M)$_{4}$As$_4$ ($M = $ Co or Ni) [16].
Those of the optimally doped \( \mu \)±NMR physical properties similar to those of Ca and K is driven by their dissimilar sizes and reduces the space group from \( \text{I4/mmm} \) in \( \text{AFe}_2\text{As}_2 \) to \( \text{P4/mmm} \) in \( \text{CaKFe}_4\text{As}_4 \) (\text{CaK1144}) 16-18]. Consequently, there are two inequivalent As sites: As1 and As2 sites close to the K and Ca layers, respectively [see, Fig. 1(a)].

**FIG. 1.** (a) Crystal structure of \( \text{CaKFe}_4\text{As}_4 \). Note the two crystallographically inequivalent As sites exist: As1 and As2 sites close to the K and Ca layers, respectively. (b)-(e) Schematic spin structures for four magnetic states associated with two magnetic wave vectors \( \mathbf{Q}_1 = (\pi,0) \) and \( \mathbf{Q}_2 = (0,\pi) \). (b) Stripe-type spin structure where \( \mathbf{M} \parallel \mathbf{Q} \). (c) Spin-charge density wave (SCDW) spin structure where \( \mathbf{M} = \pm \mathbf{M}_2 \). (d) Loop-type spin-vortex crystal spin structure with \( \mathbf{M} \perp \mathbf{Q} \). (e) Hedgehog-type spin-vortex crystal spin structure where \( \mathbf{M} \parallel \mathbf{Q} \). The wine-colored arrows on the blue spheres (iron sites) represent the directions of Fe magnetic moments. The arrows on the As sites indicate the direction of the internal magnetic induction \( \mathbf{B}_{\text{int}} \) for each As site. No arrow on the As sites correspond to zero internal magnetic induction. Note that (1) \( \mathbf{B}_{\text{int}} \) is finite at both the As sites and is oriented along c axis for the orthorhombic stripe-type antiferromagnetic state (b), (2) \( \mathbf{B}_{\text{int}} \) is finite at the both the As sites and is in \( ab \) plane for SCDW state (c), (3) \( \mathbf{B}_{\text{int}} \) is zero at the both the As sites for the loop-type SVC state (d), and (4) \( \mathbf{B}_{\text{int}} \) is finite along the c axis at the As1 site while \( \mathbf{B}_{\text{int}} \) is zero at the As2 site for the hedgehog-type SVC state (e).

The parent compound \( \text{CaKFe}_4\text{As}_4 \) (\( x = 0 \)) is a superconductor with the transition temperature \( T_c = 35 \text{K} \) [17] and a very high upper critical field about 92 T [17] with no other phase transition from 1.8 K to room temperature and shows physical properties similar to those of the optimally doped \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \). The multiband nature of the compound and \( s^\pm \) nodeless two-gap SC state has been revealed by such as nuclear magnetic resonance (NMR) [19], muon spin relaxation (\( \mu \)SR) [20], scanning tunneling microscopy (STM) [21], high-resolution angle-resolved photoemission spectroscopy (ARPES) [22], and neutron scattering [23] measurements as well as density functional theory (DFT) calculations [22]. With Ni substitution for Fe in \( \text{CaK(Fe}_{1-x}\text{Ni}_x)\text{As}_4 \), \( T_c \) decreases from 35 K at \( x = 0 \) to 10 K at \( x = 0.049 \), and the new hedgehog SVC magnetic state appears by \( x = 0.033 \) with a Neel temperature (\( T_N \)) of 45 K which increases to 52 K at \( x = 0.049 \) [16].

Quite recently, the intrinsic coexistence of the hedgehog SVC antiferromagnetic and superconducting states in the \( x = 0.049 \) (\( T_N = 52 \text{K}, T_c = 10 \text{K} \)) compound has been revealed by \( ^{75} \text{As} \) NMR measurements [24]. Motivated by the observation of the hedgehog SVC in
CaK(Fe_{0.951}Ni_{0.049})_4As_4 by NMR, we have carried out $^{75}$As NMR study in $x = 0.33$ ($T_N = 45$ K, $T_c = 23$ K) to investigate the Ni substitution effect on hedgehog SVC state in CaK(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ from a microscopic point of view.

**Experimental**

Single crystals of CaK(Fe$_{0.967}$Ni$_{0.033}$)$_4$As$_4$ (3.3%Ni-CaK1144) ($T_N = 45$ K, $T_c = 23$ K) for the NMR measurements were grown out of a high-temperature solution rich in transition metals and arsenic [16,18,25]. NMR measurements of $^{75}$As ($I = 3/2$, $\gamma_N/2\pi = 7.2919$ MHz/T, $Q = 0.29$ barns) nuclei were conducted using a laboratory-built phase-coherent spin-echo pulse spectrometer. In situ ac magnetic susceptibility ($\chi_{ac}$) was measured by monitoring the resonance frequency $f$ of the NMR coil tank circuit as a function of temperature ($T$) using a network analyzer. The $^{75}$As-NMR spectra were obtained by sweeping the magnetic field $H$ at a fixed frequency $f = 53.0$ MHz.

**Results and discussion**

Figures 2(a) and 2(b) show the typical external magnetic field-swept $^{75}$As-NMR spectra of 3.3%Ni-CaK1144 at $f = 53.0$ MHz in the paramagnetic and the antiferromagnetic states for two magnetic field directions, the $H \parallel c$ axis and $H \parallel ab$ plane, respectively. For comparison, similar $^{75}$As NMR spectra observed in 4.9%Ni-CaK1144 ($x = 0.049$) are also shown in Figs. 2(c) and 2(d). The NMR spectrum for a nucleus with spin $I = 3/2$ with Zeeman and quadrupolar interactions can be described by a nuclear spin Hamiltonian [26],

$$\mathcal{H} = -\gamma_N h (1 + K) H I_z + \frac{I_z^2 + I^2}{6}$$

where $H$ is the external field, $h$ is Planck's constant, $K$ is the Knight shift, and $I_z$ is the nuclear quadrupole frequency. The nuclear quadrupole frequency for $I = 3/2$ nuclei is given by $v_Q = eQV_{ZZ}/2h$, where $Q$ is the nuclear quadrupole moment and $V_{ZZ}$ is the electric field gradient at the As site. When the Zeeman interaction is greater than the quadrupolar interaction, this Hamiltonian produces an NMR spectrum with a sharp central transition line flanked by one satellite peak on either side.

As observed in $^{75}$As NMR spectra measurements in $x = 0$ and 0.049 [16,18,24], the two sets of $I = 3/2$ quadrupole split lines, corresponding to the two inequivalent As sites in the paramagnetic state, are observed as shown in Fig. 2. The lower field central peak with a greater Knight shift $K$ (and also larger quadrupole frequency, $v_Q$) has been assigned to the As2 site close the Ca layers and the higher field central peak with a smaller $K$ (and also smaller $v_Q$) has been attributed to the As1 site close to the K layers [19]. The clear separation of the two As NMR lines indicates that the well ordered K and Ca layers are not disturbed by Ni substitution, as has been pointed out in the case of $x = 0.049$ previously [24].

Figures 3 (a) and 3(b) show the $T$ dependence of $K_{ab}$ ($H \parallel ab$ plane), $K_c$ ($H \parallel c$ axis) and $v_Q$ for the two As sites, together with the corresponding data for $x = 0$ and 0.049. The $K$-values at the As2 site are uniformly higher than $K$-values at the As1 site over the full temperature range. Due to the poor signal intensity at high temperature, $v_Q$ and $K_{ab}$ can only be determined precisely up to 150-200 K. On the other hand, $K_c$ can be measured up to 300 K since $K_c$ can be determined from the peak position of the central transition line with no need of $v_Q$ values. For both the As sites, the $K$-values are nearly independent of temperature, and also nearly independent of Ni substitution, indicating that static uniform magnetic susceptibility is nearly independent of both temperature and $x$, although the ground states vary from magnetic to nonmagnetic. These data also suggest that Ni substitution up to 4.9% does not produce significant change in the density of states at the Fermi energy $N(E_F)$. 
The temperature dependences of $\nu_Q$ of As1 and As2 of 3.3%Ni-CaK1144 are similar to those of $\nu_Q$ of the As sites in pure CaK1144 [19] and 4.9%Ni-CaK1144 [24], as shown in Fig. 3(c). For the As1 site, with increasing temperature, $\nu_Q$ increases from 12.0 MHz at 25 K to 12.7 MHz at 150 K, while the As2 site shows an opposite trend where $\nu_Q$ decreases from 14.85 MHz at 25 K to 14.1 MHz at 150 K. As seen in the figure, we observed no abrupt change in $\nu_Q$ across $T_N$, indicating no structural transition at the magnetic phase transition. The first-principles analysis shows the different $T$ dependences of $\nu_Q$’s for the two As sites can be explained by hedgehog SVC magnetic fluctuations [19].

FIG. 2. Typical field-swept $^{75}$As-NMR spectra of CaK(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ in the paramagnetic state (upper panel) and the hedgehog spin-vortex crystal antiferromagnetic state (lower panel) for (a) the $H \parallel c$ axis ($x = 0.033$), (b) the $H \parallel ab$ plane ($x = 0.033$), (c) the $H \parallel c$ axis ($x = 0.049$), and (d) the $H \parallel ab$ plane ($x = 0.049$). The insets in (a) and (c) enlarge the central transition around 7.2 T and 5.9 T, respectively. Magenta and blue curves represent simulated spectra for As1 and As2, respectively. The dark green lines at the lower panel represent the sum of the simulated spectra. Expected lines above 8.3 T are not measured due to the limited maximum magnetic field for our SC magnet.
When temperature is lowered below \( T_N = 45 \) K, for the \( H \parallel c \) axis, each line of 3.3\%Ni-CaK1144 starts to broaden and the observed spectra become more complex, as typically shown in the lower panel of Fig. 2(a). Similar complex NMR spectra have been observed in the magnetically ordered state for the 4.9\%Ni-CaK1144 sample as also shown in the lower panel in Fig. 2(c) [24]. In the case of \( H \parallel c \) axis, each NMR line from the As1 sites splits into two lines (total 6 lines) due to internal magnetic induction \( B_{\text{int}} \), whereas no splitting of the NMR line for the As2 sites is observed. Here, it is noted that the different \( v_Q \) value for each As site makes unambiguous peak assignments of the complicated spectrum in the antiferromagnetic state possible. When \( H \) is applied parallel to the \( ab \) plane, in contrast, no splitting for the As1 NMR line is observed, as shown in Fig. 2(b). Again, as shown in Fig. 2(d), the similar no-splitting behavior of \(^{75}\text{As}\) NMR spectra has been observed in the 4.9\%Ni-CaK1144 sample below \( T_N \).

The difference in the NMR spectra for the different magnetic field can be simply explained by taking the direction of \( B_{\text{int}} \) for the As sites. The effective magnetic induction \( B_{\text{eff}} \) is given by the vector sum of \( B_{\text{int}} \) at the As site and \( H \), i.e., \( |B_{\text{eff}}| = |B_{\text{int}} + H| \). Therefore, when \( B_{\text{int}} \) is parallel or antiparallel to \( H \), \( B_{\text{eff}} = H \pm B_{\text{int}} \) and a splitting of each line is expected. On the other hand, when \( H \) is perpendicular to the \( B_{\text{eff}} \), no splitting of the line is expected since \( B_{\text{eff}} \) is expressed by \( B_{\text{eff}} = (H^2 + B_{\text{int}}^2)^{0.5} \). Thus, doubling the resonance lines at the As1 site only for \( H \parallel c \) clearly shows that \( B_{\text{int}} \) at the As1 site is oriented along the \( c \) axis. The absence of a clear splitting or shift of the resonance lines associated with the As2 site below \( T_N \) indicates the net \( B_{\text{int}} \) at the As2 sites is zero for both \( H \) directions. Since this hyperfine field pattern is consistent with the hedgehog SVC [see, Fig. 1(e)], one can conclude that the hedgehog-type SVC antiferromagnetic state is realized in the 3.3\%Ni-CaK1144 sample below \( T_N = 45 \) K. The line broadening indicates that \( B_{\text{int}} \) is slightly distributed, probably originating from the distributions of the Fe ordered moments. It is noted that no NMR signal from the paramagnetic impurity phase can be observed, indicating a high quality of the sample.

Below \( T_c \), we observe a strong reduction of NMR signal intensity due to the Meissner effect, which makes spectrum measurements difficult in the SC state. The values of \( T_c \) for both \( H \) directions were determined by measuring the temperature dependence of the NMR coil tank circuit resonance frequency, \( f_{\text{tune}} \). The frequency \( f_{\text{tune}} \) is a measure of the ac-susceptibility \( \chi_{ac} \) since \( f_{\text{tune}} = 1/2\pi (LC)^{0.5} \) and \( L = L_0 (1 + \chi_{ac}) \). Here \( L \) and \( C \) are inductance and capacitance, respectively, of the NMR coil tank circuit. The onset of the Meissner effect therefore results in a sharp change of \( f_{\text{tune}} \) as shown in Fig. 3(d). \( T_c \) decreases to 21.4 and 20.0 K for the application of \( H = 7.2 \) T along the \( ab \) plane and the \( c \) axis, respectively, from \( T_c \sim 22.8 \) K under \( H = 0 \). The difference in the reduction of \( T_c \) for the two \( H \) directions is due to an anisotropy of upper critical field \( H_{c2} \), and the anisotropy parameter \( \eta(T) = H_{c2}^a(T)/H_{c2}^c(T) \) is estimated to be \( \sim 2 \) near \( T_c \), which is comparable to that in the pure CaK1144 [18] ad also in 4.9\%Ni-CaK1144 [24]. Since we do not observe any trace of paramagnetic impurity phases in the NMR spectrum below \( T_N \), we can exclude a possibility of phase separation in the compound. Therefore, we conclude the intrinsic coexistence of the hedgehog SVC and SC states in the 3.3\%Ni-CaK1144 sample.

Finally, let us discuss the temperature dependence of \( B_{\text{int}} \) at the As1 site in the hedgehog-type SVC antiferromagnetic state. The \( B_{\text{int}} \) determined from the splitting of the As1 central line for \( H \parallel c \) axis in 3.3\%Ni-CaK1144 decreases slightly from 1.25 kOe at \( T = 20 \) K to 1.20 kOe at 25 K. Figure 3(c) shows the temperature dependence of \( B_{\text{int}} \), together with the data for the 4.9\%Ni-CaK1144 sample with \( T_N = 52 \) K. The horizontal axis of Fig. 3(c) is normalized by \( T_N \) to compare the \( T \) dependence of \( B_{\text{int}} \) for the two different compounds. With the change in \( T_N \) from 52 K for \( x = 0.049 \) to 45 K for \( x = 0.033 \), no clear difference in \( B_{\text{int}} \) is observed. Although we could not measure \( B_{\text{int}} \) close to \( T_N \) for 3.3\%Ni-CaK1144 due to poor signal intensity, the temperature dependence of \( B_{\text{int}} \) above \( T_c \) seems to be the same with the case of 4.9\%Ni-CaK1144 where \( B_{\text{int}} \) starts to increase rapidly and saturates at low \( T \), consistent with the second-order phase transition. A similar temperature dependence has been
observed in the hyperfine field at the Fe sites from Mössbauer measurements above $T_c$. [16].

Summary

We have carried out $^{75}$As-NMR measurements to investigate the magnetic properties of the magnetic superconductor CaK(Fe$_{0.967}$Ni$_{0.033}$)$_4$As$_4$ from a microscopic point of view. The new magnetic structure the so-called hedgehog-type spin-vortex crystal (SVC) antiferromagnetic state is clearly demonstrated by the direct observation of internal magnetic induction along the $c$ axis at the As1 site (close to K) and a zero net internal magnetic induction at the As2 site (close to Ca) below an AFM ordering temperature $T_N \sim 45$ K. The NMR signal intensity are strongly reduced due to Meissner effect below $T_c \sim 23$ K, indicating the intrinsic coexistence of the hedgehog-type SVC antiferromagnetic and superconducting state in $x = 0.033$. Similar intrinsic coexistence has been observed in $x = 0.049$ [24]. On the other hand, such a coexistence has not been observed in 1.7%Ni-CaK1144 ($x = 0.017$) which exhibits only superconductivity below $T_c = 31$ K [16], indicating the magnetic phase boundary must be located between $x = 0.017$ and 0.033. It is interesting to determine the magnetic phase boundary in this system. Further detailed experiments on samples between $x = 0.017$ and 0.033 are required to establish the more detailed phase diagram of CaK(Fe$_{1-x}$Ni$_x$)$_4$As$_4$. 

![FIG. 3. (a) Temperature dependences of the $^{75}$As-NMR shifts $K_c$ and $K_{ab}$ for the As1 and As2 sites for $x = 0.033$. The $K_c$ and $K_{ab}$ data for $x = 0$ and 0.049 are from Refs. [18] and [24], respectively. (b) Temperature dependence of quadrupole frequency $\nu_Q$ for the As1 and the As2 sites, estimated from the NMR spectra. $\nu_Q$’s for $x = 0$ and 0.049 are from Refs. [18] and [24]. (c) Temperature dependence of the internal magnetic induction $B_{int}$ for the As1 site in the magnetic ordered state for the $H \parallel c$ axis as a function of the normalized temperature by $T_N$. The data for $x = 0.049$ are from Ref. [24]. The curve is a guide to the eyes. (d) Temperature dependence of the resonance frequency $f_{\text{tune}}$ of the NMR tank circuit.](image-url)
Acknowledgements

We thank P. Wiecki, K. Rana, R. Fernandes, P. Orth, I. Mazin, A. Kreyssig, V. Borisov, and R. Valentí for helpful discussions. The research was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. Ames Laboratory is operated for the US Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358. W.R.M. was supported by the Gordon and Betty Moore Foundation’s EPiQS Initiative through Grant No. GBMF4411.

Present address: Karlsruhe Institute of Technology, Institut für Festkörperphysik, 76021 Karlsruhe, Germany.

References


