Probing the superconducting properties of the Si-doped Nb-oxynitride superconductor $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$

A. D. Hillier,[1] Y. Ohashi,[2] S. Kikkawa,[2] and J. V. Yakhmi[3]

[1]*ISIS Facility, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Oxfordshire OX11 0QX, United Kingdom*

[2]*Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo 060-8628, Japan*

[3]*Homi Bhabha National Institute, Anushaktinagar, Mumbai-400 094, India*

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The superconducting state of the 17 K Si-doped Nb-oxynitride superconductor, namely, $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$, has been investigated using muon spin rotation and relaxation. Our results show that there is no evidence of time-reversal symmetry breaking and that the temperature dependence of the magnetic penetration depth is consistent with an isotropic singlet "*s*-wave" ground state. The magnetic penetration depth has been determined to be 218(5) nm and the superconducting gap was found to be 3.4(1) meV, giving a BCS ratio of 4.6. The superelectron density and effective mass were found to be 8.7×10^{27} m^{-3} and $15m_e$, respectively. Also, using the Uemura plot, it is suggested that the mechanisms for superconductivity in this material may not be entirely conventional and could be similar to the cuprates, organics, and heavy fermion systems.

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I. INTRODUCTION

The search for new superconductors has resulted in surprising new families of materials, such as the pnictides, high temperature superconductors, borocarbides, etc. However, in trying to understand these superconductors, it is often useful to look for universal correlations between some of the fundamental properties, the investigation of which may lead to a classification scheme. One such scheme is the so-called "Uemura plot" in which a correlation has been proposed between T_C and the effective Fermi energy T_F, under which the exotic superconductors, such as cuprate, heavy fermion, organic, fullerene, and Chevrel phase superconductors, all follow a similar linear trend with values of $1/100 < T_C/T_F < 1/10$, in contrast to the conventional BCS superconductors (Nb, Sn, Al, etc.) for which $T_C/T_F < 1/1000$ [1,2]. Niobium is an elemental superconductor, which shows type II behavior [3], and doping niobium with nitrogen leads to some interesting properties [4–10], and, depending on the structure formed, the superconducting transition temperature can be enhanced up to 17.7 K for the rocksalt δ-NbN, or suppressed, for example, 4 K for α-NbN_x. Recently, oxynitrides of Nb and cation-doped oxynitrides of Nb have been shown to exhibit enhanced values of T_C.

The quaternary tantalum oxynitrides, e.g., $SrTaO_2N$ and $LaTaON_2$, are known to be nonsuperconducting dielectric perovskites [11–17]. However, the quaternary niobium oxynitrides $(Nb_{0.95}Mg_{0.05})(N_{0.92}O_{0.08})$, $(Nb_{0.89}Al_{0.11})(N_{0.84}O_{0.16})$, and $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ not only crystallize in a rocksalt structure [18–23], but these niobium oxynitrides also exhibit remarkably high superconducting transition temperatures of up to $\approx$17 K, with shielding volume fractions ranging between 90% and 100%. In addition to the high superconducting transition temperature, the critical current density (J_C) for the Si-doped sample, estimated from the isothermal magnetic hysteresis, was $\approx 2.5 \times 10^4$ A/cm^2 at 5 K, nearly four times higher than the corresponding values for Mg- or Al-doped samples, which was suggested to arise possibly because the cationic vacancies induced by silicon doping act as additional pinning centers in the rocksalt structure [21]. Heat capacity measurements also showed strong correlations for the Si-doped sample, as reflected by a high value of the Sommerfeld constant γ ($\approx$25 mJ/mol K^2), in contrast with much lower values of γ for the Mg-doped and the Al-doped samples (0.1798 and 3 mJ/mol K^2, respectively), where the parameter γ stands for the coefficient for the electronic contribution to the heat capacity in the equation $C = \gamma T + \beta T^3$ [21]. One could say that the Mg- and Al-doped samples behaved as nearly "free electron" systems. The T_C value of the Si-doped niobium oxynitride $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ decreased gradually from 16.8 K to around 11 K under an increasing applied magnetic field of up to 14 T [24]. This relatively small T_C reduction under an applied magnetic field suggests a robustness of its superconducting behavior in comparison to that in the parent niobium oxynitride. Both Si *K*-edge x-ray absorption near edge structure (XANES) and ^{29}Si magic angle spinning (MAS)-NMR indicated that the local structure of pinning centers around the silicon atoms close to cationic vacancies was similar to that of Si in amorphous SiO_2 in the rocksalt structure of niobium oxynitride $Nb(N_{0.87}O_{0.13})$ [24].

Muon spin rotation (μSR) has proven itself to be an extremely powerful tool in probing the superconducting properties of any material [25–28]. The fundamental superconducting parameters, namely, the penetration depth λ and coherence length ξ, can be determined using muon spin rotation data. Using these results, together with heat capacity data, the superfluid density n^* and effective mass m^* can also be determined [26]. Moreover, muon spin relaxation has been shown to be very useful at looking for unconventional superconductivity, for example, looking for superconductors that break time-reversal symmetry, as in Sr_2RuO_4, $PrOs_4Sb_{12}$, $LaNiC_2$, and $LaNiGa_2$, among others [29–36]. In view of the interesting superconducting behavior exhibited by the

Si-doped $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ superconductor, we decided to undertake a μSR study of this sample and report our results in what follows. Our results show that there is no evidence of time-reversal symmetry breaking and that the temperature dependence of the magnetic penetration depth is consistent with an isotropic singlet "*s*-wave" ground state. The magnetic penetration depth has been determined to be 218(5) nm and the superconducting gap was found to be 3.4(1) meV, giving a BCS ratio of 4.6.

II. EXPERIMENTAL DETAILS

The sample preparation details were described in our previous publication [24]. Briefly, $NbCl_5$ (Sigma-Aldrich, 99.9%) was dissolved with $Si(OC_2H_5)_4$ (Aldrich, 98.0%) at a molar ratio of 9:1 in anhydrous ethanol, along with an equimolar amount of citric acid (Wako Pure Chemicals) for the preparation of $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$. The viscous material was fired at 350 °C for 1 h in air, and the resultant oxide powder was ground. The amorphous oxide precursor was nitrided in an alumina boat with ammonia (Sumitomo Seika Chemicals, 99.9%), and annealed at 1200 or 1500 °C for 3 h under 0.5 MPa N_2 in a graphite furnace (High Multi 500, Fuji Dempa Kogyo). The sample used in this study was that used in the previous study [24].

The μSR experiment was carried out on about 1.3 g powder of a Si-doped Nb-oxynitride superconducting sample $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ using the MuSR spectrometer [32] in both geometries [longitudinal/zero field (LF/ZF-μSR) and transverse field (TF-μSR)]. At the ISIS Facility, a pulse of muons is produced every 20 ms and has a full width at half maximum (FWHM) of ≈70 ns, but with one in five pulses going to the ISIS second target station. These muons are implanted into the sample and decay with a half-life of 2.2 μs into a positron which is emitted preferentially in the direction of the muon spin axis and two neutrinos. These positrons are detected and time stamped in the detectors which are positioned before, F, and after, B, the sample for longitudinal (relaxation) experiments. Using these counts the asymmetry in the positron emission can be determined and, therefore, the muon polarization is measured as a function of time. For the transverse field experiments, the magnetic field was applied perpendicular to the initial muon spin direction and momentum. The sample was powdered and mounted onto a 99.995+% pure silver plate in a Ag package. Any muons which stop in silver give a time independent background for ZF-μSR experiments or a nondecaying precession signal in TF-μSR. The sample holder and sample were mounted into a cryostat with a temperature range of 1.2–300 K. The sample was cooled to base temperature in zero field and the μSR spectra were collected upon warming the sample while still in zero field. The stray fields at the sample position are canceled to within 1 μT by a flux-gate magnetometer and an active compensation system controlling three pairs of correction coils. The TF-μSR experiment was conducted with applied fields of 40 mT, which ensured the sample was in the mixed state. The field was applied above the superconducting transition before cooling. The MuSR spectrometer comprises 64 detectors. In software, each detector is normalized for the muon decay and reduced into two orthogonal components.

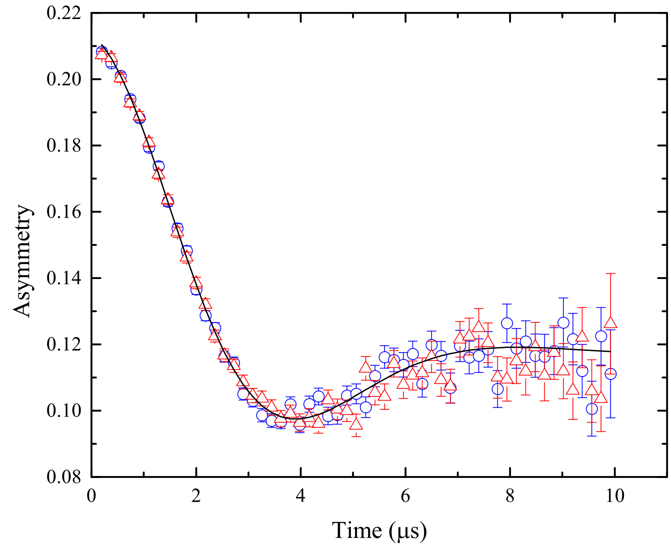

FIG. 1. (Color online) The zero-field μSR spectra for $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$. The red symbols are the data collected at 1.5 K and the blue symbols are the data collected at 20 K. The line is a fit to the data using the model described in the text.

III. RESULTS

We first consider the zero-field μSR data. The absence of a precession signal in the μSR spectra at all temperatures confirms that there are no spontaneous coherent internal magnetic fields associated with long range magnetic order in $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ at any temperature. In the absence of atomic moments the muon spin relaxation is expected to arise entirely from the local fields associated with the nuclear moments. These nuclear spins are static, on the time scale of the muon precession, and randomly orientated. In this case, the depolarization function $G_z(t)$ can be described by the Kubo-Tayabe function [37],

$$G_z^{\mathrm{KT}}(t) = A_0\left[\frac{1}{3} + \frac{2}{3}(1-\sigma^2t^2)\exp\left(-\frac{\sigma^2t^2}{2}\right)\right] \times \exp(-\lambda t) + C, \quad (1)$$

where A_0 is the initial asymmetry, σ is the muon depolarization rate and is related to the field width at the muon site, λ is for any electronic contribution (in this case negligibly small), and C is the background. In Fig. 1, we can see that the data have the characteristic shape of the Kubo-Toyabe function, with a depolarization rate of 0.436(1) and 0.436(3) μs^{-1} for low and high temperatures, respectively. More importantly, this does not change as a function of temperature. This indicates that time-reversal symmetry is preserved, i.e., not broken, or at least any symmetry breaking field is not observable by μSR. In an applied transverse magnetic field the experimental data were fitted with a sinusoidal oscillating function with a Gaussian relaxation component,

$$G_x(t) = \sum_{i=1}^{2} A_i \exp\left(-\frac{\sigma_i^2t^2}{2}\right)\cos(2\pi\nu_i t + \varphi), \quad (2)$$

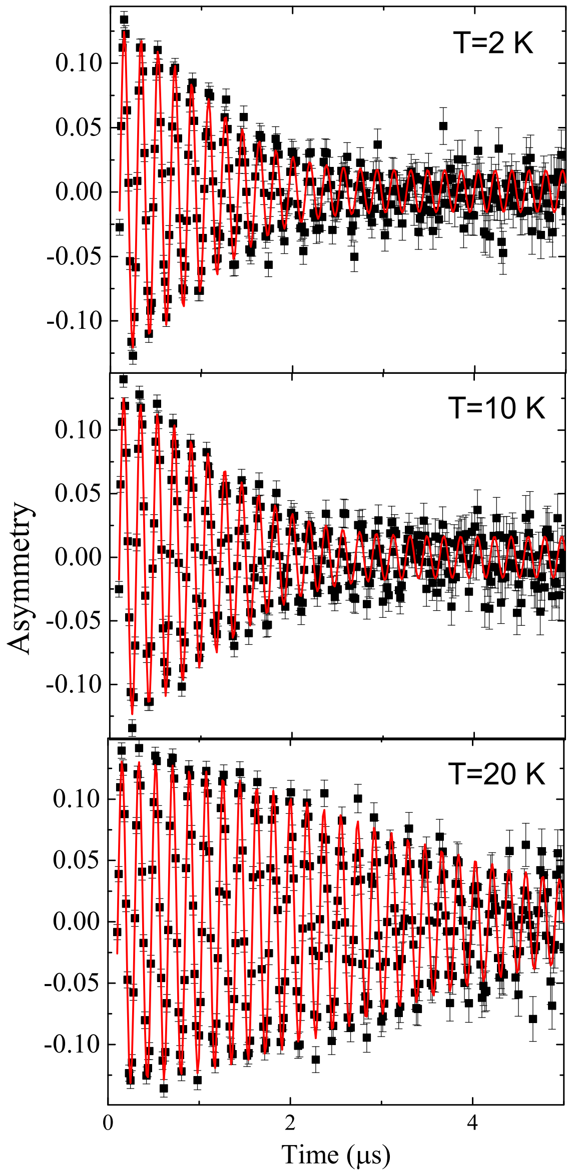

FIG. 2. (Color online) Typical muon asymmetry spectra in $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ taken in a transverse field of 40 mT at 2.0 (upper), 10.0 (middle), and 20.0 K (lower). The line is a fit to the data (see text). For clarity, only one of the two virtual detectors has been shown.

where the index i denotes the contribution from the superconducting phase or the background, respectively, A_i is the initial asymmetry, σ_i is the Gaussian relaxation rate, ν_i is the muon spin precession frequency, and φ is the phase offset. The background term comes from those muons which were implanted into the silver sample holder, and this oscillating term has no depolarization, i.e., $\sigma_2 = 0.0\ \mu s^{-1}$, as silver has a negligible nuclear moment. Figure 2 shows typical spectra and fits for $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ with an applied field of 40 mT at 2.0, 10.0, and 20.0 K after being field cooled through T_C. Figure 3 shows the temperature dependence of σ_1. This shows an increase as the temperature is reduced through T_C. σ is directly related to λ by the relation

$$\sigma_{sc} = A(1-b)[1+1.21(1-\sqrt{b})^3]\lambda^{-2}, \qquad (3)$$

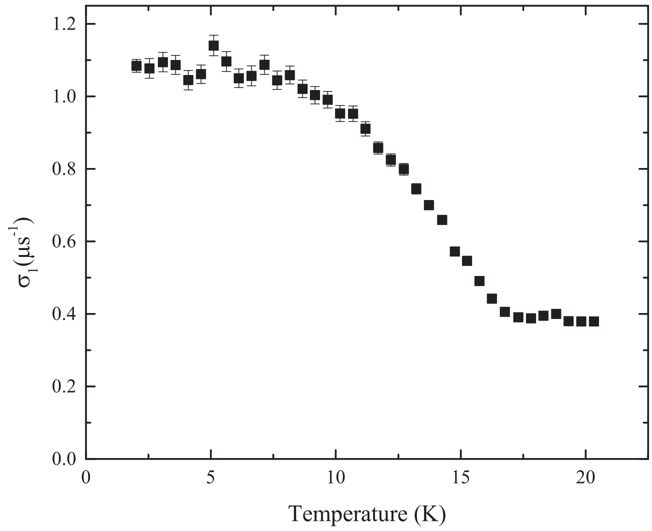

FIG. 3. The temperature dependence of σ_1 in a field of 40 mT.

where $b = B/B_{c2}$ is the ratio of applied field to the upper critical field and A is a prefactor relating to the structure of the flux line lattice ($A = 4.83 \times 10^4$ and 5.07×10^4 for a hexagonal and square lattice, respectively) [38,39]. As B_{c2} is large relative to the applied field, we can assume that $\sigma \propto 1/\lambda^2$. Considering the values for σ_1 as $T \to 0$, the magnetic penetration depth can be determined, assuming a hexagonal flux line lattice, to be $\lambda = 218(5)$ nm. Now we present a detailed analysis of the $\sigma_{sc}(T)$. The σ_1 value measured in the superconducting state σ_{sc} is a convolution of both the flux line lattice and the nuclear moments σ_N such that $\sigma_1 = \sigma_{sc}^2 + \sigma_N^2$. The contribution from the nuclear moments has been determined at a temperature just above T_C and has been assumed to be constant. This assumption is justified by the zero-field μSR experiment discussed earlier. As σ_{sc} is directly related to the magnetic penetration depth, the superconducting gap can be modeled by

$$\frac{\sigma_{sc}(T)}{\sigma_{sc}(0)} = \frac{\lambda^{-2}(T)}{\lambda^{-2}(0)} = 1 + 2\int_{\Delta(T)}^{\infty}\left(\frac{\partial f}{\partial E}\right)\frac{E}{\sqrt{E^2-\Delta(T)^2}}dE, \qquad (4)$$

where $f = [1+\exp(E/k_BT)]^{-1}$ is the Fermi function [40]. The temperature dependence of the gap was approximated by [41]

$$\Delta(T) = \Delta(0)\tanh\{1.82[1.018(T_C/T-1)]^{0.51}\}. \qquad (5)$$

As can be seen from Fig. 4, the temperature dependence of σ_{sc} is very well described by an isotropic s-wave model, giving $\Delta(0) = 3.4(1)$ meV and a BCS ratio of 4.6, which is in agreement with heat capacity results [24]. This value is slightly higher than that expected for a conventional BCS superconductor, indicating that $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ may exhibit enhanced electron-phonon coupling.

The magnetic penetration depth λ is related directly to two of the principal parameters of the electronic ground state of a material, namely, the effective mass of the electron m^* and the carrier density n_s. Moreover, the heat capacity is also related to n_s and m^*. For more details, see Hillier *et al.* [26].

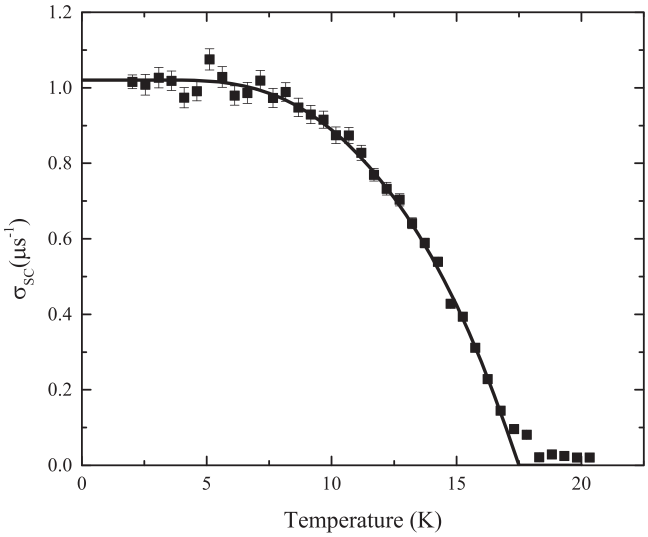

FIG. 4. The temperature dependence of the $\sigma_{sc}(T)$. The line is a fit to the data using an isotropic s-wave model (see text for details).

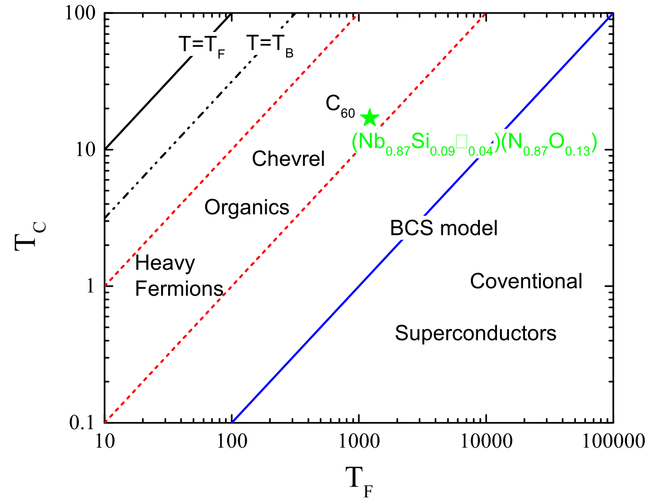

FIG. 5. (Color online) The "Uemura plot," which shows a classification scheme for conventional and "unconventional" superconductors. The green star shows the position of $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ within this scheme and suggests that the mechanisms for superconductivity may not be entirely conventional.

Therefore, by using a combination of the muon results and the heat capacity, the n_s and m^* were found to be 8.7×10^{27} m^{-3} and $15m_e$, respectively.

Uemura *et al.* [1,2] have suggested a classification scheme for unconventional superconductors which shows a correlation between T_C and the effective Fermi energy T_F in which the exotic superconductors, such as cuprate, heavy fermion, organic, fullerene, and Chevrel phase superconductors, all follow a similar linear trend with $1/100 < T_C/T_F < 1/10$, in contrast to the conventional BCS superconductors (Nb, Sn, Al, etc.) for which $T_C/T_F < 1/1000$. The "Uemura plot" of $\log(T_C)$ against $\log(T_F)$ is shown in Fig. 5 and appears to discriminate dramatically between the "exotic" and "conventional" superconductors. If we assume the clean limit and if the superelectron at $T = 0$ K is equivalent to carrier density at T_C, T_F for $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ is $\approx$1220 K. This gives a T_C/T_F ratio of 1/71, which readily classifies this superconductor in the exotic region on the "Uemura plot."

IV. CONCLUSIONS

In conclusion, μSR experiments have been carried out on $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$. The zero-field measurements do not show any spontaneous fields appearing below the superconducting transition temperature ($T_C = 16.8$ K). This provides convincing evidence that time-reversal symmetry is not broken in the superconducting state of this material. Also, we have probed the superconducting gap and found that the temperature dependence of the superconducting gap can be described by an isotropic s-wave gap with a $T = 0$ K amplitude of $\Delta(0) = 3.4(1)$ meV and a BCS ratio of 4.6. This value is slightly higher than that expected for a conventional BCS superconductor, indicating that $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ might be exhibiting unconventional superconductivity. Indeed, using the "Uemura plot" to classify this superconductor, we find that $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ sits among the cuprate, heavy fermion, organic, fullerene, and Chevrel phase superconductors, suggesting that the mechanisms for superconductivity may not be entirely conventional. Clearly, this indicates that the mechanisms for superconductivity in this family of materials should be investigated further.

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[1] Y. J. Uemura, L. P. Le, G. M. Luke, B. J. Sternlieb, W. D. Wu, J. H. Brewer, T. M. Riseman, C. L. Seaman, M. B. Maple, M. Ishikawa *et al.*, Phys. Rev. Lett. **66**, 2665 (1991).

[2] Y. Uemura, Physica C **185-189**, 733 (1991).

[3] D. Herlach, G. Majer, J. Major, J. Rosenkranz, M. Schmolz, W. Schwarz, A. Seeger, W. Templ, E. H. Brandt, U. Essmann *et al.*, Hyperfine Interact. **63**, 41 (1991).

[4] R. W. Guard, J. W. Savage, and D. G. Swarthou, Trans. Metall. Soc. AIME **239**, 643 (1967).

[5] E. F. Skelton, M. R. Skokan, and E. Cukauskas, J. Appl. Crystallogr. **14**, 51 (1981).

[6] P. Fabbricatore, P. Fernandes, G. Gualco, F. Merlo, R. Musenich, and R. Parodi, J. Appl. Phys. **66**, 5944 (1989).

[7] B. Scheerer, J. Cryst. Growth **49**, 61 (1980).

[8] R. Berger, W. Lengauer, and P. Ettmayer, J. Alloys Compd. **259**, 9 (1997).

[9] A. Linde, R.-M. Marin-Ayral, D. Granier, F. Bosc-Rounessac, and V. Grachev, Mater. Res. Bull. **44**, 1025 (2009).

[10] N. Terao, J. Less-Common Met. **23**, 159 (1971).
[11] G. Tobías, J. Oró-Solé, D. Beltrán-Porter, and A. Fuertes, Inorg. Chem. **40**, 6867 (2001).
[12] Y.-I. Kim, P. M. Woodward, K. Z. Baba-Kishi, and C. W. Tai, Chem. Mater. **16**, 1267 (2004).
[13] Y. Zhang, T. Motohashi, Y. Masubuchi, and S. Kikkawa, J. Ceram. Soc. Jpn. **119**, 581 (2011).
[14] Y. Zhang, T. Motohashi, Y. Masubuchi, and S. Kikkawa, J. Eur. Ceram. Soc. **32**, 1269 (2012).
[15] D. Logvinovich, L. Bocher, D. Sheptyakov, R. Figi, S. Ebbinghaus, R. Aguiar, M. Aguirre, A. Reller, and A. Weidenkaff, Solid State Sci. **11**, 1513 (2009).
[16] M. Yashima, M. Saito, H. Nakano, T. Takata, K. Ogisu, and K. Domen, Chem. Commun. **46**, 4704 (2010).
[17] D. Oka, Y. Hirose, H. Kamisaka, T. Fukumura, K. Sasa, S. Ishii, H. Matsuzaki, Y. Sato, Y. Ikuhara, and T. Hasegawa, Sci. Rep. **4**, 4987 (2014).
[18] S. Yamamoto, Y. Ohashi, Y. Masubuchi, T. Takeda, T. Motohashi, and S. Kikkawa, J. Alloys Compd. **482**, 160 (2009).
[19] Y. Ohashi, T. Motohashi, Y. Masubuchi, and S. Kikkawa, J. Solid State Chem. **183**, 1710 (2010).
[20] Y. Ohashi, T. Motohashi, Y. Masubuchi, T. Moriga, K. Murai, and S. Kikkawa, J. Solid State Chem. **184**, 2061 (2011).
[21] Y. Ohashi, S. Kikkawa, I. Felner, M. Tsindlekht, D. Venkateshwarlu, V. Ganesan, and J. Yakhmi, J. Solid State Chem. **188**, 66 (2012).
[22] L. Clark, J. Oró-Solé, K. S. Knight, A. Fuertes, and J. P. Attfield, Chem. Mater. **25**, 5004 (2013).
[23] A. Miura, T. Takei, N. Kumada, S. Wada, E. Magome, C. Moriyoshi, and Y. Kuroiwa, Inorg. Chem. **52**, 9699 (2013).
[24] Y. Ohashi, Y.Masubuchi, D. Venkateshwarlu, V. Ganesan, J. Yakhmi, T.Yoshida, and S. Kikkawa, J. Solid State Chem. **210**, 238 (2014).
[25] R. C. S. L. Lee and S. H. Kilcoyne, *Muon Science: Muons in Physics, Chemistry and Materials* (SUSSP/IOP, London, 1998).
[26] A. Hillier and R. Cywinski, Appl. Magn. Res. **13**, 95 (1997).
[27] A. Schenck, *Muon Spin Rotation* (Hilger, Bristol, 1985).
[28] J. Sonier, Rep. Prog. Phys. **70**, 1717 (2007).
[29] G. M. Luke, A. Keren, L. P. Le, W. D. Wu, Y. J. Uemura, D. A. Bonn, L. Taillefer, and J. D. Garrett, Phys. Rev. Lett. **71**, 1466 (1993).
[30] G. M. Luke, Y. Fudamoto, K. M. Kojima, M. I. Larkin, J. Merrin, B. Nachumi, Y. J. Uemura, Y. Maeno, Z. Q. Mao, Y. Mori *et al.*, Nature (London) **394**, 558 (1998).
[31] Y. Aoki, A. Tsuchiya, T. Kanayama, S. R. Saha, H. Sugawara, H. Sato, W. Higemoto, A. Koda, K. Ohishi, K. Nishiyama *et al.*, Phys. Rev. Lett. **91**, 067003 (2003).
[32] A. D. Hillier, J. Quintanilla, and R. Cywinski, Phys. Rev. Lett. **102**, 117007 (2009).
[33] A. D. Hillier, J. Quintanilla, B. Mazidian, J. F. Annett, and R. Cywinski, Phys. Rev. Lett. **109**, 097001 (2012).
[34] A. Maisuradze, W. Schnelle, R. Khasanov, R. Gumeniuk, M. Nicklas, H. Rosner, A. Leithe-Jasper, Y. Grin, A. Amato, and P. Thalmeier, Phys. Rev. B **82**, 024524 (2010).
[35] P. K. Biswas, H. Luetkens, T. Neupert, T. Stürzer, C. Baines, G. Pascua, A. P. Schnyder, M. H. Fischer, J. Goryo, M. R. Lees *et al.*, Phys. Rev. B **87**, 180503(R) (2013).
[36] L. Shu, W. H. Y. Aoki, A. D. Hillier, K. Ohishi, K. Ishida, R. Kadono, A. Koda, O. O. Bernal, D. E. MacLaughlin, Y. Tunashima *et al.*, Phys. Rev. B **83**, 100504(R) (2011).
[37] R. S. Hayano, Y. J. Uemura, J. Imazato, N. Nishida, T. Yamazaki, and R. Kubo, Phys. Rev. B **20**, 850 (1979).
[38] E. Brandt, J. Low Temp. Phys. **73**, 355 (1988).
[39] E. H. Brandt, Phys. Rev. B **68**, 054506 (2003).
[40] M. Tinkham, *Introduction to Superconductivity* (Krieger, Malabar, FL, 1975).
[41] A. Carrington and F. Manzano, Physica C **385**, 205 (2003).