Absence of pure quadrupole ordering in $SmSn_3$: Dipole-dipole and quadrupole-quadrupole interactions in Sm-based compounds

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The intermetallic cubic compound $SmSn_3$ is currently the only candidate for pure quadrupole ordering among existing Sm-based compounds. In this paper, we report on magnetic susceptibility and muon spin relaxation measurements on $SmSn_3$ and demonstrate that a spontaneous local magnetic field appears in the ordered state, which undoubtedly rules out the pure quadrupole ordering. Dipole-dipole and quadrupole-quadrupole interactions in trivalent lanthanide systems are discussed on the basis of a de Gennes theory, indicating that the former tends to dominate in Sm intermetallics. This also provides a general guideline for future searches of quadrupole-related phenomena in trivalent lanthanide systems.

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I. INTRODUCTION

Lanthanide and actinide compounds exhibit a variety of physical properties originating from f-electrons' spin and orbital degrees of freedom (DOF). These are systematically expressed with multipole moments, namely, magnetic dipoles, electric quadrupoles, and magnetic octupoles, etc. Recent theoretical and experimental efforts have revealed that not only the dipole but also higher-order multipoles play an essential role in f-electron systems. For instance, multiple ordered phases and their anomalous response to magnetic field H in CeB_6 were successfully explained on the basis of competition and interplay of various multipole interactions.[1] Furthermore, novel superconductivity coexisting with antiferroquadrupole (AFQ) ordering was recently found in $PrIr_2Zn_{20}$, suggesting the Cooper pairing mediated by quadrupole fluctuations.[2] Thus, detailed understanding of multipole interactions is of growing importance in modern f-electron physics.

Early researches on multipole ordering and related phenomena were conducted intensively in Ce^{3+} systems with a f^1 configuration for simplicity. Now, researchers' interest gradually extends over f^n systems with $n \geqslant 2$. In this paper, we focus on Sm^{3+} systems with a f^5 configuration and discuss competitive nature of multipole interactions, especially between dipole-dipole (DD) and quadrupole-quadrupole (QQ) interactions. The Sm^{3+} ion is characterized by the total angular momentum $J = 5/2$ as well as the Ce^{3+} ion. Thus, a degenerated crystalline-electric-field (CEF) ground state with quadrupole DOF is possibly realized. However, pure quadrupole ordering has not been established in Sm-based compounds yet.

A series of SmX_3 (X = In, Sn, Pb, Tl, Pd) are known to have the Γ_8 CEF ground state with dipole, quadrupole, and octupole DOF.[3–5] Among these compounds, a possibility of pure quadrupole ordering and successive antiferromagnetic (AFM) phase transitions have been proposed in $SmIn_3$ and $SmSn_3$ from an analogy with the successive phase transitions in CeB_6.[3] Recently, a muon spin relaxation (μSR) study ruled out the pure quadrupole ordering in $SmIn_3$ by detecting a spontaneous local field.[6] Thus, $SmSn_3$ is currently the only candidate for the pure quadrupole ordering in existing Sm-based compounds and detailed investigation of $SmSn_3$ is necessary in order to discuss the competitive nature of DD and QQ interactions in Sm-based compounds in general. This compound crystallizes into the $AuCu_3$-type cubic structure. Specific heat C in zero applied field (ZF) shows a broad peak at $T_{\rm I} \sim 10.8$ K and two sharp peaks at $T_{\rm II} \sim 10.3$ K and $T_{\rm III} \sim 9.6$ K, indicating successive phase transitions.[3] Magnetic entropy was evaluated to be $R\ln 2.5$ at 11 K, increasing gradually to $R\ln 3.7$ at 30 K. These features resemble those of CeB_6, implying that the CEF ground state of $SmSn_3$ is the Γ_8 quartet. Magnetic susceptibility shows a cusp-like anomaly at around 12 K, suggesting an AFM ground state.[7] The temperature dependence of elastic constants C_{11}, C_{44}, and $(C_{11} - C_{12})/2$ also exhibits anomalies at $T_{\rm I}$, $T_{\rm II}$, and $T_{\rm III}$ together with another anomaly at $T_{\rm IV} \sim 6.1$ K.[4] A marked elastic softening was observed in the $(C_{11} - C_{12})/2$ mode above $T_{\rm I}$, indicating that the quadrupole DOF are active in the CEF ground state. No magnetic hyperfine splitting in ^{119}Sn Mössbauer spectra was observed well below the phase transition temperatures.[8] The possible magnetic splitting is probably masked by the quadrupole splitting observed both in the paramagnetic and the ordered phases. Electrical resistivity shows a dense Kondo behavior, which is rare in Sm-based compounds.[3] Thermal expansion also exhibits anomalies at the phase transition temperatures.[3] These gradually shift toward higher temperature with increasing H, as was observed in typical AFQ ordering systems CeB_6,[9] $PrPb_3$,[10] and TmTe.[11] As mentioned above, Kasaya *et al*. proposed pure quadrupole ordering at $T_{\rm I}$ and AFM transitions at $T_{\rm II}$ and $T_{\rm III}$ to explain the successive phase transitions in the Γ_8 subspace.[3] However, no microscopic evidence of the pure quadrupole ordering has been obtained yet.

ZF-μSR is an ideal probe to distinguish the primary order parameter into magnetic and electric multipoles from a microscopic point of view. In this paper, we report on magnetic susceptibility and μSR measurements on $SmSn_3$ and demonstrate that the primary order parameters in all the ordered phases are a magnetic multipole (most probably a magnetic dipole), contrary to the pure quadrupole ordering scenario. From a semiquantitative discussion on the strength of the DD and QQ interactions in trivalent lanthanide (Ln^{3+})

systems, it will be shown that the former tends to dominate in the Sm^{3+} case. This also provides a general guideline for future searches of novel quadrupole-related phenomena in Ln^{3+} systems.

II. EXPERIMENTAL RESULTS

A single-crystalline sample of $SmSn_3$ was prepared by the Bridgeman method. Magnetic susceptibility of $SmSn_3$ was measured using a SQUID magnetometer (MPMS, Quantum Design, Inc.) in H up to 5 T applied along the [001] direction. ZF-μSR measurements were carried out at the D1 area (J-PARC MUSE, Japan), using spin-polarized pulsed muon beam with a double-pulse structure at the interval of $\delta = 0.60\,\mu$s. Single-crystalline samples of $SmSn_3$ were moderately crushed and randomly aligned on a silver cold plate in order to maximize the cross-sectional area of the samples for the pulsed μSR experiment. The time-differential μSR data $AP(t)$ were recorded over the temperature range 2.7–100 K with a conventional ^{4}He flow cryostat, where A is the full asymmetry and $P(t)$ is the projection of muon spin polarization $\boldsymbol{P}(t)$ onto the muon incident axis.

The temperature dependence of the magnetic susceptibility $\chi(T)$ in the paramagnetic state is typical of the Sm^{3+} ion and consistent with a previously reported data.[5,7] Figure 1 displays $\chi(T)$ below 14 K down to 2 K. $\chi(T)$ exhibits a broad maximum at $T^* = 12.0$ K and gradually decreases with decreasing temperature. The T^* anomaly should be comparable with the broad peak at $T_{\rm I} = 10.8$ K in $C(T)$. Anomalies corresponding to the successive phase transitions are found at $T_{\rm II} = 9.9$ K and $T_{\rm III} = 9.4$ K. The upturn below 5.5 K should be intrinsic since this persists even in high H and seems to be related to the elastic anomaly at $T_{\rm IV}$. In addition, a new anomaly is found at $T'_{\rm III} = 9.0$ K, also observed by ZF-μSR as mentioned later. This can be identified with a kink in the temperature dependence of C_{44} at ~9.0 K[4]. The inset shows the H-T phase diagram

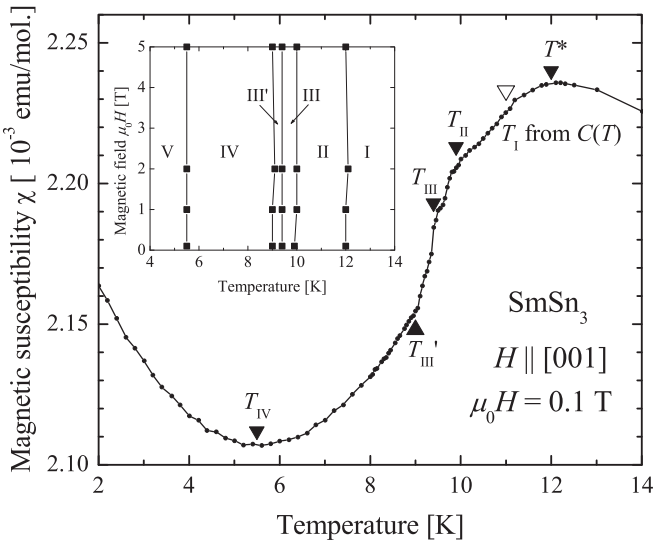

FIG. 1. Temperature dependence of magnetic susceptibility $\chi(T)$ in $SmSn_3$ below 14 K in a magnetic field of 0.1 T applied along the [001] direction. The inset shows the H-T phase diagram extracted from $\chi(T)$.

in H||[001] extracted from the $\chi(T)$ anomalies. The phase boundary between phase I and II was determined from T^*. All the phase transition temperatures are almost constant against H, at least up to 5 T. This seems to contradict the $dT_{\rm I}/dH > 0$ behavior in the previously reported thermal expansion data.[3]

Figure 2(a) shows ZF-μSR spectra in $SmSn_3$ below 15.8 K. A background signal from the silver cold plate has been subtracted. A full amplitude signal from the samples with $A = 0.080$ exhibits nearly temperature-independent slow relaxation well above T^*, primarily due to the nuclear dipole moment of ^{117}Sn and ^{119}Sn and fluctuating Sm magnetic moment. An exponential-shaped fast relaxation component appears below ~T^* and the fractional weight of the fast relaxation component p gradually increases with decreasing temperature. We also performed longitudinal field (LF) μSR measurements to clarify the origin of the fast relaxation in the ZF-μSR spectra. The μSR spectra at 10.6 K in the phase II under ZF and several LFs are shown in Fig. 2(b). The nearly flat tail after the early-time fast relaxation in LFs proves that the fast relaxation is primarily caused by a spontaneous *static* local magnetic field $B_{\rm loc}$.[12] The long-time slow relaxation component gradually increases in amplitude with applied LF, denoting a decoupling of the muon spin from $B_{\rm loc}$. These results distinctly indicate that the primary order parameter in phase (II) is not the electric quadrupole but a magnetic multipole.

In order to extract detailed information about the magnetically ordered phases, we used the following function to analyze the ZF-μSR data:

$$AP(t) = A\frac{G(t) + e^{-\frac{\delta}{\tau_\mu}}G(t+\delta)}{1 + e^{-\frac{\delta}{\tau_\mu}}}, \tag{1}$$

$$G(t) = pe^{-\lambda_1 t} + (1-p)e^{-\lambda_2 t}, \tag{2}$$

where $\tau_\mu = 2.2\,\mu$s is the muon life time, and $\lambda_{1,2}$ is the relaxation rate. The double-pulse structure of the muon beam was taken into account in accordance with the treatment given in Ref. 13. The fast relaxation component is exclusively ascribed to the muons stopped in magnetically ordered volume of the sample. On the other hand, the slow relaxation component is derived from muons in two different environments. A part originates from the magnetically ordered volume and this dominates below $T_{\rm I}$. The remain of the slow relaxation component comes from the muons in the paramagnetic volume and this dominates above $T_{\rm I}$. For the sake of convenience, we do not distinguish these and just treat these as an exponentially relaxing component. The best fits with Eq. (1) are represented in Fig. 2(a) with solid curves. The temperature dependence of p and $\lambda_{1,2}$ obtained from the fits is shown in Figs. 2(c) and 2(d), respectively. Note that only the λ_1 smaller than $10\mu s^{-1}$ is displayed in view of the pulsed muon time-resolution ~0.1 μs. The influence of successive phase transitions most clearly appears in p. The temperature dependence of p indicates that the magnetic volume fraction increases below T^* with decreasing temperature and levels off at $T_{\rm I} = 11.0$ K. Successive anomalies are found at $T_{\rm II}$, $T_{\rm III}$, and $T'_{\rm III}$, although no distinct feature is observed at $T_{\rm IV}$. The temperature variation in p below $T_{\rm I}$ probably reflects sequential changes of magnetic

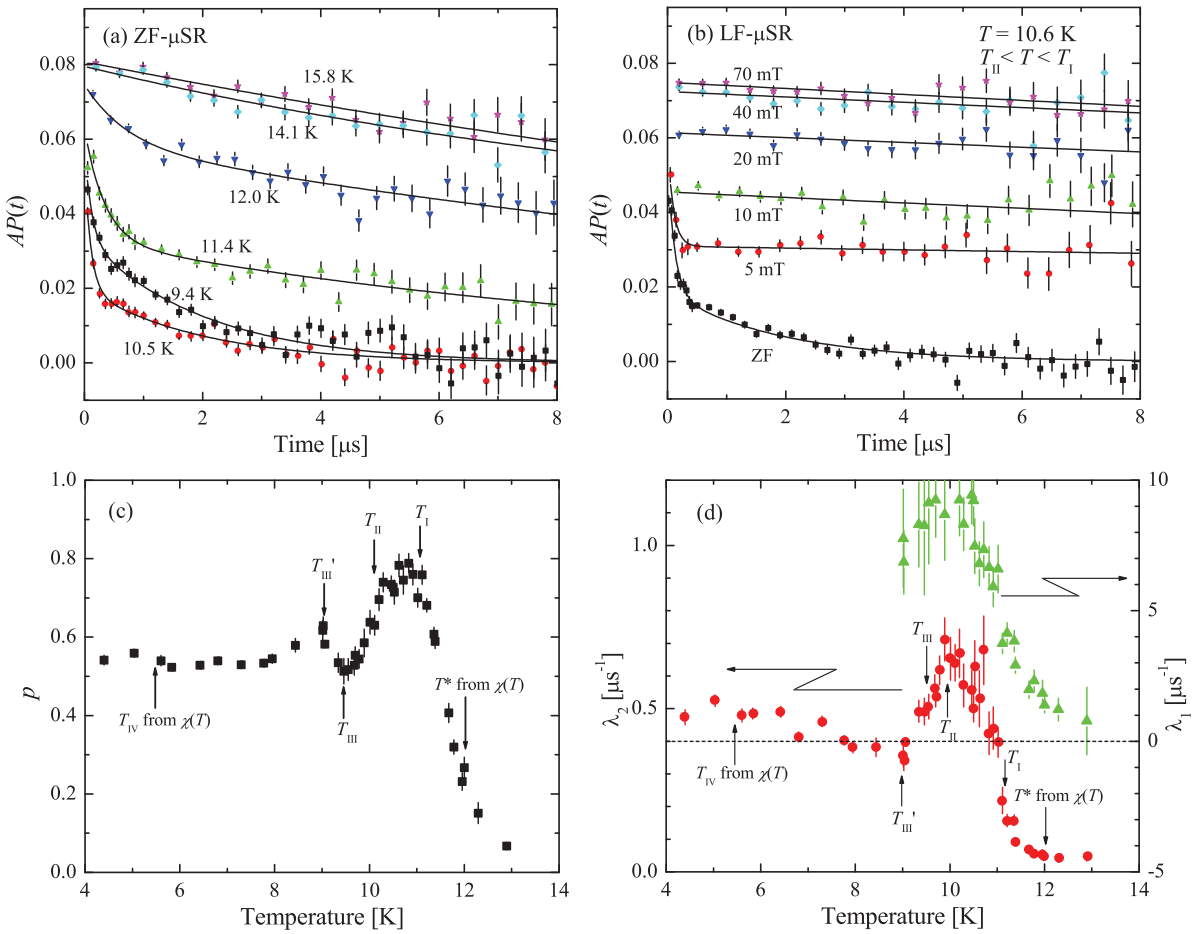

FIG. 2. (Color online) (a) ZF-μSR spectra in $SmSn_3$ at several temperatures between 9.4 and 15.8 K. The solid curves represent the best fits with Eq. (1). (b) LF-μSR spectra in $SmSn_3$ at several LFs at 10.6 K in the phase II. (c) p in ZF as a function of temperature. (d) λ_1 and λ_2 in ZF as functions of temperature.

structure associated with the successive phase transitions. p should decrease when the muon site with $B_{\rm loc}\sim 0$ is populated in a certain magnetically ordered phase as a result of accidental cancellation of the hyperfine field. In addition, a direction of $B_{\rm loc}$ can affect p as well since the orientation of the moderately crushed single crystals might not be completely random.

III. DISCUSSION

We now discuss the order parameter and magnetic structure in $SmSn_3$ and the relative strength of DD and QQ interactions in Ln^{3+} systems in general. Our experimental results clearly demonstrate that the primary order parameter in phase II and the other ordered phases is a magnetic multipole and contradicts the pure quadrupole ordering scenario.[3] In addition, the $dT_1/dH > 0$ behavior, which was the basis of the pure quadrupole ordering scenario, is not evident in our $\chi(T)$ data. Thus, we conclude that the primary order parameter is most probably a magnetic dipole. The gradual variation in $p(T)$ at $\sim T^*$ suggests a spatial distribution of the phase transition temperature of the phase II in the specimen. This may indicate that the quadrupole moment plays an important role in phase II as a *secondary* order parameter, which should be sensitive to sample quality. Note that the insensitivity of the phase boundaries to H does not contradict to the primary AFM ordering since the magnitude of the Sm magnetic dipole moment is small ($0.53\mu_B$ in the Γ_8 subspace). A high H $\sim$30 T is required for the Zeeman splitting energy overcoming the spontaneous DD interaction $\sim$10 K. This is beyond the magnetic field range accessible with standard scientific instruments like the MPMS. This argument is not restricted to $SmSn_3$ but can be generally applied to AFM Sm-based compounds, which typically show the AFM ordering of $4f$-dipole moment at $\sim$10 K.

The muon stopping site in the $AuCu_3$-type crystal has been established as the $3d$ site (Wycoff notation) from muon Knight shift measurements on isomorphic Pr-based compounds.[14,15] Since this site locates at the midpoint of two nearest neighbor Sm ions in $SmSn_3$, the hyperfine field is canceled out when two magnetic dipole moments are symmetric with respect to the muon site. Thus, the simple AFM structure with the magnetic propagation vector $\boldsymbol{q} = (1/2,1/2,1/2)$ is ruled out because the nonzero $B_{\rm loc}$ was observed by ZF-μSR in all the ordered phases. It is difficult to determine the detailed magnetic structure only from the present ZF-μSR data so that magnetic diffraction techniques are required.

The present result undoubtedly rules out the pure quadrupole ordering in $SmSn_3$, which has been the only

candidate for the pure quadrupole ordering in existing Sm-based compounds. Many Sm-based compounds possess the CEF ground state with quadrupole DOF. Nevertheless, why does the DD interaction tend to overcome the QQ interaction in Sm-based compounds? Last, we discuss the relative strength of the DD and QQ interactions in Sm^{3+} and other Ln^{3+} ions on the basis of the LS coupling scheme[16–18] in order to understand this trend. We here consider a metallic system in which the DD and QQ interactions are mediated via an isotropic RKKY interaction and the coupling between multipole moments of a single lanthanide ion and a molecular field from surrounding ions for simplicity. Therefore, ferroquadrupole (FQ) ordering, where the order parameter strongly couples with macroscopic lattice deformation, is beyond this model and only AFQ ordering will be covered. The following argument also presupposes a degenerated or pseudo-degenerated CEF ground state, including both dipole and quadrupole DOF.

In metallic compounds, it is known that the spin exchange interaction mediated by conduction electrons predominates the DD interaction and its strength is approximately proportional to the square of the total spin of $4f$-electrons $\boldsymbol{S}^2$.[19,20] The de Gennes factor $dG = (g_J - 1)^2 J(J+1)$ is the alternative representation of $\boldsymbol{S}^2$ with the good quantum number J, where g_J is the Lande g factor. We adopt dG as a scalar to indicate the strength of the DD interaction. Actually, a good linear scaling between dG and magnetic phase transition temperatures was experimentally observed in lanthanide metals.[19] Here, we ignore the influence of the orbital angular momentum $\boldsymbol{L}$ for simplicity, which contributes mainly to the anisotropy of the DD interaction.[21] Figure 3(a) shows dG as a function of the number of f-electrons n_f in the Ln^{3+} ions. The closed and open symbols represent Kramers and non-Kramers ions, respectively. Note that the non-Kramers ion systems possibly have a CEF ground state without dipole DOF.

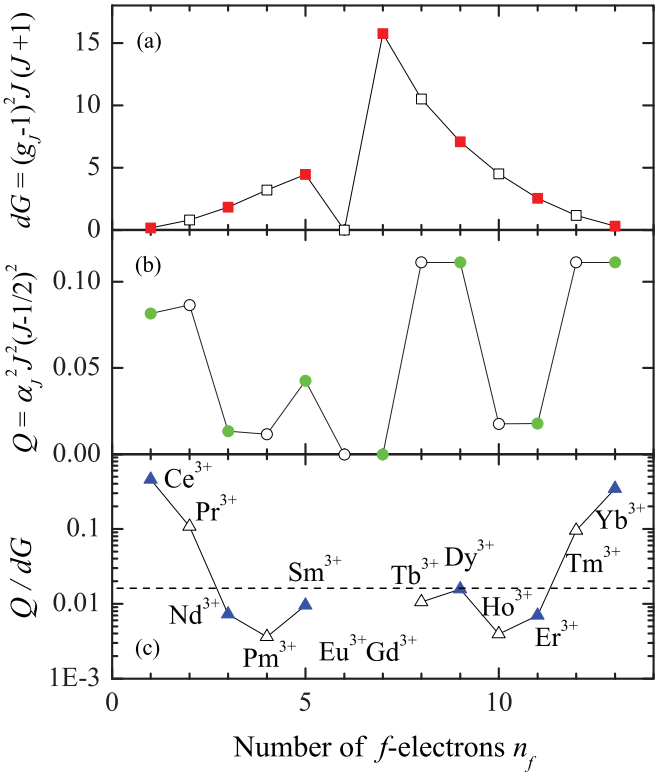

FIG. 3. (Color online) (a) dG, (b) Q, and (c) Q/dG for Ln^{3+} ions. The closed and open symbols represent Kramers and non-Kramers ions, respectively.

On the other hand, the strength of the QQ interaction should be proportional to the square of the product of the second order Stevens factor α_J and the expectation value of a quadrupole operator.[22] We choose the Γ_{3g}-type quadrupole moment O_0^2 as a representative of five quadrupole moments and use its maximum value $J(J-1/2)$ to evaluate the quadrupole coupling strength. The characteristic index of the quadrupole coupling $Q = \alpha_J^2 J^2 (J-1/2)^2$ is plotted in Fig. 3(b) as a function of n_f. Q is large on both sides and for Tb^{3+} and Dy^{3+}, while Q for Sm^{3+} is intermediate. The especially large Q for Dy^{3+} is consistent with the highest AFQ ordering temperature of 24.7 K in DyB_2C_2[23] that ever was observed.

We are now ready to compare the relative strength of the QQ interaction over the DD interaction using the ratio of the characteristic scalars Q/dG as shown in Fig. 3(c). The dashed line divides Ln^{3+} ions into two groups. Pure AFQ ordering has been experimentally detected only for the ions in the upper region with Q/dG larger than for Dy^{3+}. This plot successfully explains the experimental trend that the pure quadrupole ordering is frequently found in the both sides of the lanthanide series. The Sm^{3+} ion places just below the threshold line. This suggests that the DD and QQ interactions are comparable in strength, but the former tends to dominate over the latter in Sm-based compounds. Note that this plot simply provides a *rough* estimation of the relative strength of the multipole interactions and does not necessarily exclude the pure quadrupole ordering in Sm-based compounds. This is possible when the quadrupole moment strongly couples with unconsidered factors, macroscopic lattice distortion, for example. Fermi surface properties can also affect the competitive nature of the multipole interactions as was observed in filled-skutterudites.[24,25] Nevertheless, this plot would keep importance as a general guideline for future searches of novel quadrupole-related phenomena in Ln^{3+} systems.

IV. CONCLUSIONS

We presented μSR and magnetization studies on $SmSn_3$, the only candidate for pure quadrupole ordering among existing Sm-based compounds. Multiple ordered phases including the possible pure quadrupole ordering phase were investigated from both microscopic and macroscopic view points. In the possible pure quadrupole ordering phase, a spontaneous local magnetic field was detected by μSR, which undoubtedly rules out the pure quadrupole ordering in $SmSn_3$. In order to understand this result, we discussed DD and QQ interactions in Ln^{3+} systems on the basis of a de Gennes theory and obtained the Q/dG vs. n_f plot, indicating that the former tends to dominate in Sm intermetallics. This also provides a general guideline for future searches of quadrupole-related phenomena in Ln^{3+} systems.

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