Nuclear quadrupole resonance study of the electronic properties of the narrow-gap semiconductor $FeSb_2$

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Electronic properties of the narrow-gap semiconductor $FeSb_2$ have been studied by the magnetization and $^{121/123}$Sb nuclear quadrupole resonance measurements. In addition to the susceptibility, the spin-lattice relaxation rate has revealed a fully opened gap at the Fermi level. The relaxation process is dominated by the magnetic contribution at high temperature T, while the quadrupole contribution becomes dominant below 70 K. Electronic field gradient at Sb sites shows anisotropic T dependence, reflecting most probably the anisotropic thermal expansion.

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Semiconductors are one of the important types of materials in developing modern electrical and computerized society. Conventional semiconductors, such as Si and GaAs, have an energy gap whose size is of the order of 10^4 K. Among strongly correlated-electron systems that show unusual electronic and magnetic properties, some kind of rare-earth and iron compounds exhibit semiconducting property.[1,2] They generally possess a narrow energy gap at the Fermi level between the bands with large density of states and a novel shaped gap is sometime observed.[1] The narrow-gap semiconductor FeSi has drawn much interest due to its anomalous thermodynamic and magnetic properties. The magnetic susceptibility χ of FeSi exhibits an activation-type behavior above 70 K, takes a broad maximum around 500 K, and decreases following the Curie-Weiss law at higher temperatures T.[2,3] Several scenarios to explain this unusual T dependence of χ have already been proposed. One is that the amplitude of local spin density fluctuations can be induced by T and saturate at high T.[4] Another is that similarly to the Kondo insulator, the energy gap may be produced by the hybridization of $3d$ states with conduction bands.[5]

$FeSb_2$ crystallizing in the marcasite-type structure (space group *Pnnm*, No. 58) was found to show similar magnetic properties to FeSi.[6,7] According to an early report, χ of $FeSb_2$ shows a paramagnetic to diamagnetic crossover below 100 K when a field H is applied along all three axes.[6] This kind of crossover was not observed for FeSi.[2] Recently, the diamagnetism at low T was observed only for the $H \| b$ axis by the experiment on large single crystals.[8] The electrical transport ρ of $FeSb_2$ is also anisotropic. For the current along either a or c axis, ρ is semiconducting over the entire T range; on the other hand, ρ of the b axis exhibits a metal-semiconductor crossover around 50 K.[6]

In this Brief Report, we report the electronic properties by the magnetization and $^{121/123}$Sb nuclear magnetic resonance (NQR) measurements in $FeSb_2$. Single crystals of $FeSb_2$ were grown from an Sb-flux method. The typical size of the crystals is $3\times3\times2$ mm^3 and each crystalline axis was determined by the x-ray Laue method. The susceptibility was measured using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-5) by a applying magnetic field up to 50 kOe. NQR measurement was carried out using a conventional phase-coherent spin-echo spectrometer. For the NQR measurement, several single crystals were crushed into powder.

Figure 1 shows the T dependence of χ of the single-crystalline $FeSb_2$. χ were measured under magnetic fields applied along the a, b, and c axes. We have measured χ of a number of single crystals. Some of them show the Curie-type upturn at low T, while others do not. This difference is probably due to the difference in the extent of lattice detects, which generally result in the paramagnetic contribution and/or the kind of impurities included in the crystals. We have found that the samples without the Curie tail show slightly nonlinear magnetization curves in a low-field range ($H<10$ kOe), indicating that impurities are of ferromagnetic type. Although the contribution of paramagnetic impurities is difficult to be estimated in χ measurements, the ferromagnetic contribution can easily be separated in magnetization measurements. Therefore, we selected the crystal which shows the least ferromagnetic component and estimated the T dependence of χ by defining $\chi \equiv dM/dH$ (M is the magnetization) at sufficiently high field up to 50 kOe. χ for three

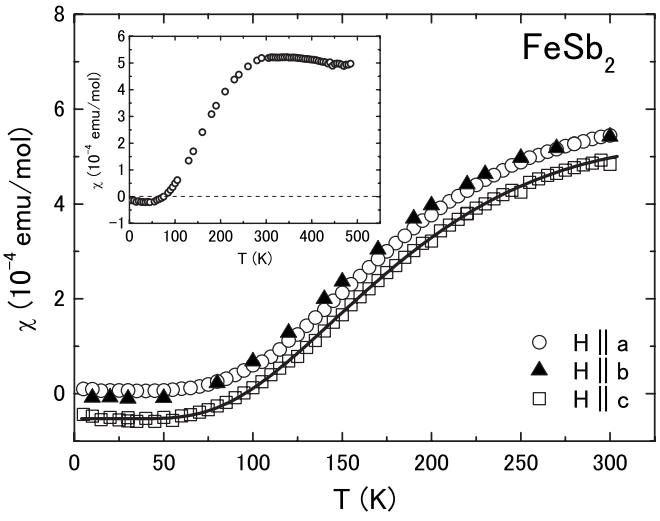

FIG. 1. Temperature dependence of the magnetic susceptibility of $FeSb_2$. The solid line indicates the best fit assuming the rectangular band model (see text). The inset shows the magnetic susceptibility of the powdered sample in a wide temperature range.

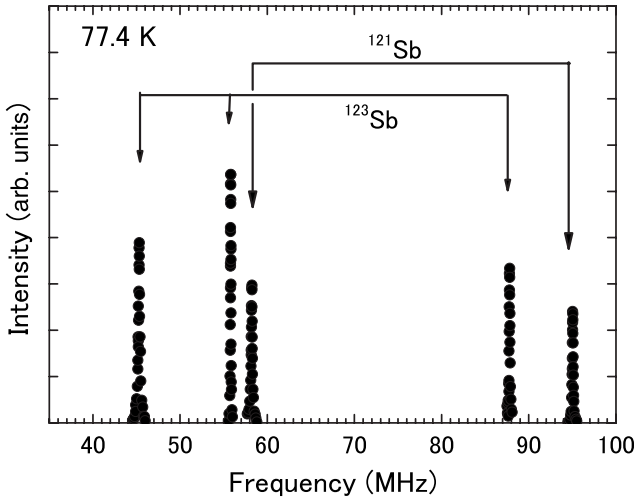

FIG. 2. $^{121/123}$Sb-NQR spectra for $FeSb_2$ at 77.4 K.

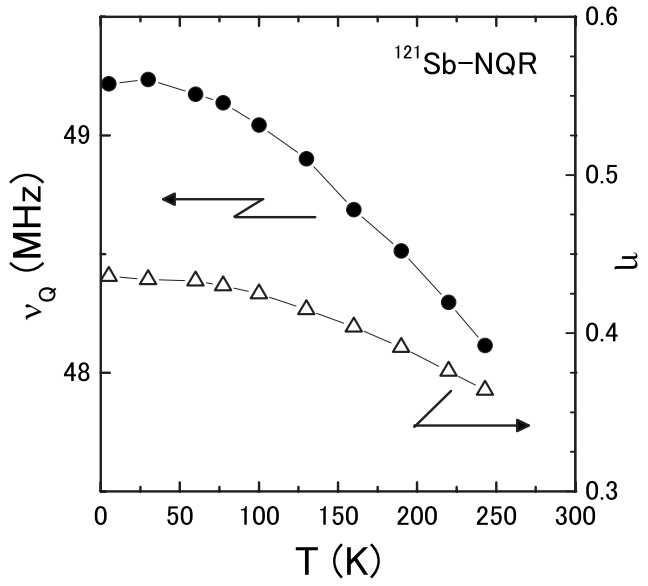

FIG. 3. Temperature dependence of NQR parameters $^{121}\nu_Q$ and η.

axes display similar T dependences as reported in Refs. 6 and 8. In the present measurement, the paramagnetic to diamagnetic crossover with decreasing T was observed for both the $H\|c$ and b axes and not for the $H\|a$ axis. This result is different from those in previous reports.[6,8] The discrepancy in the low T behavior of χ is probably ascribed to the nonlinear nature of M because χ measured at particular H depends on H. The low T diamagnetic susceptibility may be ascribed to the large core diamagnetism of the Sb atom. It should be noted that χ for all axes in the present sample does not show a Curie tail at low T. On the other hand, for itinerant electron compounds with a narrow gap, such as FeSi and YMn_4Al_8,[3,9] the Curie-type upturn at low T has always been observed, which is often ascribed to extrinsic paramagnetic impurities. In the case of $FeSb_2$, however, χ does not show such an upturn and becomes T independent at low T. This fact emphasizes that $FeSb_2$ can be a good material to study physical properties of a unique correlated-electron gap system. χ of a powdered sample was measured up to 490 K and shown in the inset of Fig. 1. The data almost agree with those in Ref. 10. The broad maximum was observed around 300 K just like the case of FeSi, but the temperature is lower than that for FeSi.

The susceptibility of an itinerant electron system with the density of states N_{eff} is given by

$$\chi(T) = -2\mu_B^2 \int N_{\text{eff}} \frac{\partial f(E,T)}{\partial E} dE, \tag{1}$$

where $f(E,T)$ is the Fermi distribution function and μ_B the Bohr magneton. Assuming N_{eff} with a gap 2Δ centered at the Fermi energy in a narrow rectangular band of width W and appending a T-independent paramagnetic susceptibility term χ_0, we performed the least-squared fit of Eq. (1) to the experimental susceptibility. Here, the fitting parameters for the $H\|c$ axis are $\Delta=420\pm20$ K, $W=230\pm30$ K, and $\chi_0=-5.3\times10^{-5}$ emu/mol. These results slightly differ from those in previous reports.[7,8] The differences are probably attributed to the different procedures to evaluate the χ. The fitting parameters for other two axes are nearly the same values as the $H\|c$ axis except for χ_0.

To elucidate the electronic structure at the microscopic level, we performed $^{121/123}$Sb-NQR measurements at zero field. Figure 2 shows NQR spectra of $^{121/123}$Sb at 77.4 K. Sb has two isotopes, ^{121}Sb and ^{123}Sb. The nuclear spin is $I=5/2$ ($I=7/2$) for ^{121}Sb (^{123}Sb) with nuclear quadrupole moment $^{121}Q \simeq -0.597\times10^{-28}$ m^2 ($^{123}Q \simeq -0.762\times10^{-28}$ m^2) and natural abundance of 57.3% (42.7%). In order to obtain the nuclear quadrupole frequency ν_Q and the nuclear asymmetry parameter η, we calculated the secular equation with Hamiltonian for the nuclear electric quadrupole interaction between the nuclear electric quadrupole moment eQ and the electric field gradient (EFG) $V_{\alpha\alpha}$ at the nuclear site. The Hamiltonian is given by

$$\mathcal{H}_Q = \frac{1}{6}\nu_Q h\left[3I_z^2 - I^2 + \frac{1}{2}\eta(I_+^2 + I_-^2)\right], \tag{2}$$

where $\nu_Q=3e^2V_{zz}Q/[2hI(2I-1)]$ and $\eta=(V_{xx}-V_{yy})/V_{zz}$ ($V_{\alpha\alpha}=\partial^2V/\partial\alpha^2, \alpha=x,y,z$). The principal components of the EFG tensors are defined as $|V_{zz}|\geqslant|V_{xx}|\geqslant|V_{yy}|$.

Using Eq. (2), we deduced from the NQR spectra $^{121}\nu_Q=49.1$ MHz ($^{123}\nu_Q=29.8$ MHz) for ^{121}Sb (^{123}Sb) and $\eta=0.43$ at 77.4 K. In fact, the ratio of $^{121}\nu_Q/^{123}\nu_Q=1.65$ is in good agreement with the theoretical values $^{121}\nu_Q/^{123}\nu_Q=1.645$ calculated from Eq. (2). T dependences of $^{121}\nu_Q$ and η are shown in Fig. 3. $^{121}\nu_Q$ increases with decreasing T and saturates below 50 K. For many noncubic metals and semimetals, ν_Q follows an empirical relation of $\nu_Q(T)=\nu_Q(0)(1-\alpha T^{3/2})$.[11] Above 80 K, $^{121}\nu_Q(T)$ of $FeSb_2$ can be described well by this relation with $^{121}\nu_Q(0)=49.4$ MHz and $\alpha=6.7\times10^{-6}$ K$^{-3/2}$. Remarkable feature in this NQR result is that η also shows a T dependent behavior as well as $^{121}\nu_Q(T)$. This is an indication that the EFG at Sb

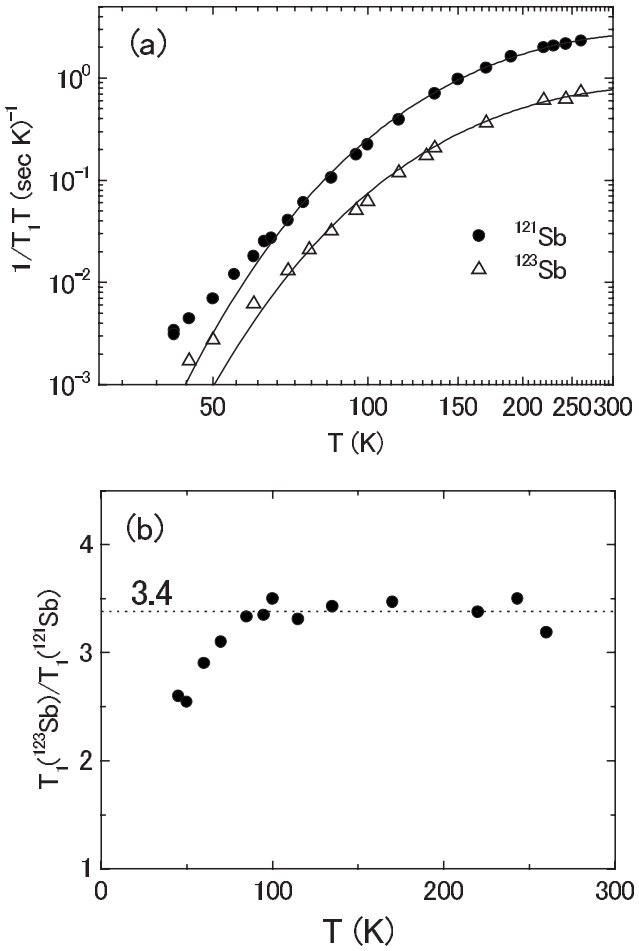

FIG. 4. (a) Temperature dependences of $1/T_1T$ in $^{121/123}$Sb. The solid curves indicate the model fit with $\Delta=446$ K and $W=230$ K. (b) Temperature dependence of the isotope ratio, $T_1(^{123}\mathrm{Sb})/T_1(^{121}\mathrm{Sb})$. The dotted line in the figure indicates the expected value when the magnetic relaxation mechanism is dominant.

sites shows an anisotropic T dependence. Each Fe atom is surrounded by a slightly distorted octahedron of Sb neighbors, two Sb with a short Fe-Sb bond distance, and four Sb with a long bond distance. The T evolution of lattice parameters is anisotropic, i.e., thermal contraction along the c axis is about six times (three times) larger than that along the a axis (b axis), and the short Fe-Sb bond distance contracts more rapidly than the long Fe-Sb bond with decreasing T.[7] The T dependence of η, i.e., the T dependence of the local symmetry of EFG at the Sb site, is a reasonable consequence of the anisotropic lattice change with T.

In order to study the energy gap of $FeSb_2$ microscopically, we measured the nuclear spin-lattice relaxation time T_1 of ^{121}Sb and ^{123}Sb between 42 and 260 K at the peak position around 95.0 and 87.8 MHz, corresponding to the $|\pm 3/2\rangle \leftrightarrow |\pm 5/2\rangle$ transition for ^{121}Sb and $|\pm 5/2\rangle \leftrightarrow |\pm 7/2\rangle$ for ^{123}Sb, respectively. Each T_1 was uniquely determined from the nuclear magnetization recovery curve using a theoretical equation in which η is incorporated.[12] Figure 4(a) shows T dependence of $1/T_1(^{123}\mathrm{Sb})$ T of ^{121}Sb and $1/T_1(^{123}\mathrm{Sb})T$ of ^{123}Sb. $1/(T_1T)$ decreases with decreasing T in the experimental T range. T dependence of $1/(T_1T)$ is generally given by

$$\frac{1}{T_1T} \propto \int N_{\mathrm{eff}}^2 \left[-\frac{\partial f(E,T)}{\partial E} \right] dE. \tag{3}$$

The experimental results at high T can be successfully reproduced by using the narrow rectangular band model with the same parameters deduced from the χ analysis. This result suggests that $FeSb_2$ has an isotropic energy gap at the Fermi surface. However, $1/(T_1T)$ deviates from the calculated curve below 70 K, although data continue to decrease with decreasing T. For semiconducting compounds with the correlated gap, the $T_1T=$const behavior was often observed at a low T region deviating from the model fitting.[13,14] The reasons have been discussed on the basis of either residual density of states inside the gap induced by extrinsic impurities or formation of spin polarons.

To explore what causes the deviation of T_1 from the fitting curve in $FeSb_2$, we plotted the isotope ratio of the relaxation rate $T_1(^{123}\mathrm{Sb})/T_1(^{121}\mathrm{Sb})$ in Fig. 4(b). $T_1(^{123}\mathrm{Sb})/T_1(^{121}\mathrm{Sb})$ shows a T-independent behavior at high T. However, that ratio decreases gradually below $\sim$80 K. In the case where the relaxation mechanism is determined by the fluctuation of the internal magnetic field at the Sb site, namely, magnetic relaxation, the isotope ratio of the relaxation time $T_1(^{123}\mathrm{Sb})/T_1(^{121}\mathrm{Sb})$ should be the squared gyromagnetic ratio $\gamma_n(^{123}\mathrm{Sb})^2/\gamma_n(^{121}\mathrm{Sb})^2 \simeq 3.4$. Meanwhile, when the relaxation mechanism is dominated by the fluctuation of the EFG at Sb sites related to the phonon and charge fluctuation, namely quadrupole, relaxation, $T_1(^{123}\mathrm{Sb})/T_1(^{121}\mathrm{Sb})$ is $^{123}Q^2f(7/2)/^{121}Q^2f(5/2) \simeq 1.5$, where the spin dependent function is given by $f(I)=(2I+3)/[I^2(2I-1)]$.[15,16] The T-independent experimental $T_1(^{123}\mathrm{Sb})/T_1(^{121}\mathrm{Sb})$ of $FeSb_2$ at high T is close to the ratio for the magnetic relaxation mechanism. Below 70 K, on the other hand, the values gradually decrease toward the quadrupole relaxation ratio with decreasing T. This is an indication that the magnetic relaxation, which is dominant at high T, is reduced and consequently the nuclear quadrupole relaxation appears to play an important role below 70 K. We, therefore, conclude that the deviation of $1/(T_1T)$ from the model fit at low T is ascribed not to the precursor of the $T_1T=$const behavior but to the gradual change in the dominant relaxation mechanism. It should be noted that the $T_1T=$const behavior associated with the residual density of states within the gap is absent down to 42 K in $FeSb_2$. Generally, the quadrupole relaxation rate is small compared with the magnetic relaxation which can be reflected by the dynamical properties of local or itinerant electron spins. In the presence of neither conduction electrons nor localized moments, however, the quadrupole process becomes dominant instead of magnetic one. Appearance of quadrupole relaxation at low T corresponds to the fact that $FeSb_2$ is a semiconductor with a nonmagnetic ground state.

In conclusion, we have reported the electronic properties of a narrow-gap semiconductor $FeSb_2$ by the magnetization and $^{121/123}$Sb-NQR measurements. T dependences of χ and T_1 are successfully explained by assuming the rectangular

bands separated by the isotropic gap opening at the Femi level. The effective band gap and band width were estimated to be $\Delta \sim 420$ K and $W \sim 230$ K, respectively. The deviation of $1/(T_1T)$ from the model fitting curve at low T is associated with the crossover of the relaxation from magnetic to quadrupole mechanism. The absence of T_1T=const behavior down to 42 K suggests the gap opening over the entire Fermi surface. Since the single crystal $FeSb_2$ with less paramagnetic impurities can be easily obtained, further studies of this compound will be helpful to understand the intrinsic properties of narrow-gap systems.

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