Spin fluctuations in the temperature-induced paramagnet FeSi

K. Tajima
Department of Physics, Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama 223, Japan

Y. Endoh
Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan

J. E. Fischer* and G. Shirane
Physics Department, Brookhaven National Laboratory, Upton, New York 11973
(Received 10 February 1988)

Extensive polarized-neutron experiments have been performed on an FeSi single crystal in a temperature range between 150 and 600 K, and the first concrete evidence that FeSi exhibits temperature-induced magnetism is presented. The magnetic scattering depends strongly on q around "ferromagnetic" reciprocal-lattice points, but the integrated intensity over energy is independent of q. The magnetic moment $M(q)$ deduced from the integrated intensity increases with increasing temperature and is in good agreement with the temperature variation of the magnetic moment calculated from the static susceptibility. The width of the energy spectrum depends strongly on both temperature and q. These results can be interpreted in terms of temperature-induced paramagnetism with a narrow-band-gap model.

I. INTRODUCTION

The cubic compound FeSi has a crystal structure of $B20$ (space group $P2_13$) and it exhibits anomalous magnetic behavior which has been studied for many years. The most unusual property is the temperature variation of the magnetic susceptibility[1] which shows a broad peak around 500 K as in Fig. 1, but no magnetic ordering has been observed down to low temperature.[2] Jaccarino *et al.*[1] proposed a semiconducting band model which has a narrow gap between conduction and valence band, as shown in the inset of Fig. 1, to reproduce the temperature dependence of the susceptibility and specific heat. The gap model was supported by the band calculation of Nakanishi *et al.*,[3] agreement with experiment being obtained only in the case of vanishing bandwidth. Takahashi and Moriya[4] claimed that this case was unrealistic for FeSi. More recently, these authors applied the self-consistent renormalization (SCR) theory developed by Moriya *et al.*[5] to the semiconducting band system and they concluded that the anomalous magnetic and thermal behavior in FeSi can be interpreted by a temperature-induced paramagnetic moment.[4,6] Evangelou and Edwards[7] also discussed the anomalous magnetism of FeSi in the temperature-induced-moment picture.

As has been pointed out by Moriya,[6] the temperature-induced magnetic moment is one of the most important characteristics in an itinerant-spin system. An appreciable temperature-induced paramagnetic moment was predicted to appear at high temperature in a weak itinerant-spin system, which has been indeed observed by Ishikawa *et al.*[8] in MnSi. The anomalous behavior of the susceptibility in some pyrite systems[9] such as CoS_2 and $CoSe_2$ is also explained by the temperature-induced moment model.

This model of temperature-induced magnetism appeared very attractive for FeSi. However, subsequent neutron scattering experiments by Motoya *et al.*[10] and Kohgi and Ishikawa[11] could not detect any trace of mag-

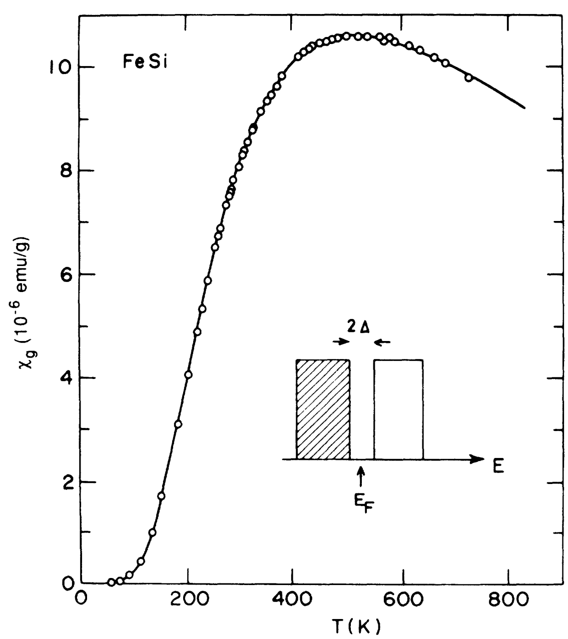

FIG. 1. The temperature dependence of the static magnetic susceptibility of FeSi [after Jaccarino *et al.* (Ref. 1)] The inset is the model of the semiconducting band structure proposed by Jaccarino *et al.* 2Δ represents the band gap between valence and conduction bands and the Fermi level E_F locates between them.

netic moment, thus failed to confirm this model. We will comment later on possible reasons for the failure of these neutron scattering experiments. The first observation of magnetic scattering was made by Ziebeck *et al.*[12] with a powder sample. However, their results are rather marginal and are interpreted as disproving the temperature induced moment model. Recent experiments with x-ray photoemission spectroscopy by Oh *et al.*[13] also gave no indication of the induced magnetic moment.

Under these circumstances, it is extremely important to reexamine the magnetic cross section in FeSi using a single crystal. We have performed neutron paramagnetic scattering experiments on FeSi with polarized neutrons using a large nearly perfect single crystal prepared for this work. This technique[14–16] is a powerful means to investigate the behavior of the magnetic moment and has been utilized extensively. The simple scattering function[17]

$$S(q,\omega)\propto M^2(q)\frac{\Gamma}{\Gamma^2+\omega^2}\ , \tag{1}$$

where $M(q)^2$ is the magnetic moment, has been shown to describe qualitatively the paramagnetic moment of various $3d$ metals.[18–20] As reported in our previous work,[21] a strong q-dependent magnetic scattering is observed

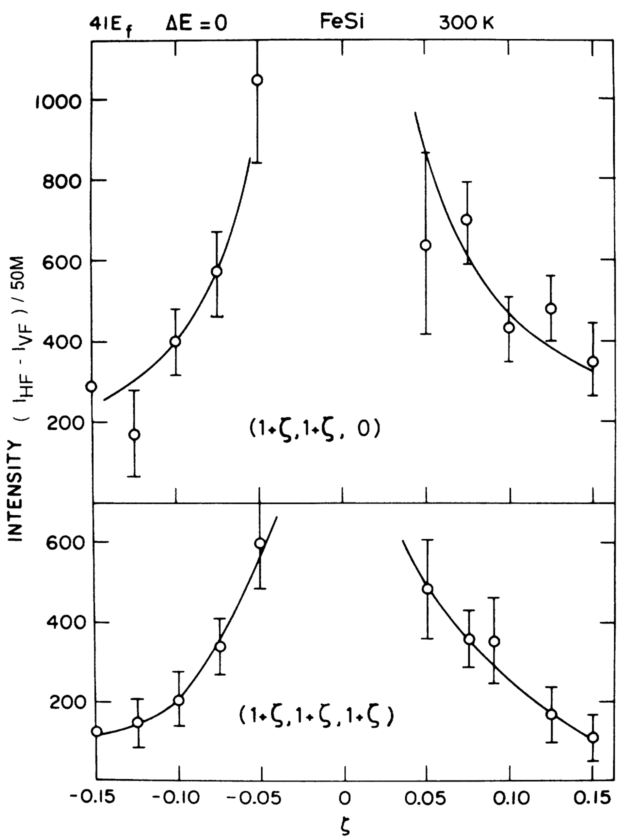

FIG. 2. The magnetic scattering observed at $(1+\zeta,1+\zeta,0)$ and $(1+\zeta,1+\zeta,1+\zeta)$ reciprocal-lattice points. The data are taken with the analyzer set at $\Delta E=0$ of 41 meV neutrons. (The energy resolution is 6 meV.) Solid lines are the guide for the eye.

around the (1,1,0) reciprocal-lattice point, as is shown in Fig. 2, and the intensity follows the temperature variation of the static susceptibility. However, the energy-integrated intensity is q independent, which is the truly unique feature of FeSi. This paper reports the experiments and analysis in detail and aims to characterize the temperature-induced magnetism.

We performed our preliminary neutron scattering experiment using a crystal of rather small size (~ 3 cm^3) and poor mosaic. However, we failed to observe the magnetic signal. The main reason was not because of the crystal. We did not find the proper experimental condition for observing $S(q,\omega)$. It should be noted that even with the new large size of crystal, observation of the magnetic scattering is not easily made because the scattering intensity is so weak and spread out in the whole Brillouin zone, as will be shown below.

II. EXPERIMENTAL RESULTS AND ANALYSIS

The polarized neutron scattering experiments were performed on a triple axis spectrometer at the High Flux Beam Reactor at Brookhaven National Laboratory. Cu_2MnAl (111) crystals were used both as monochromator and analyzer. The constant-q data were mainly taken with a fixed final energy of $E_f=41$ meV, while some of the data were taken with $E_f=60$ meV. The horizontal collimation was 40′-80′-80′-130′. The large single crystal (~ 12 cm^3) with a mosaic of about 0.3° was grown by the Czochralski method at Tohoku university. No significant second phase was detected by x-ray diffraction. The paramagnetic scattering intensities can be separated from other nuclear scattering by taking the intensity difference between the measuring modes with a horizontal field (HF) and a vertical field (VF) present at the sample site with a spin flipper on $(+-)$,

$$\frac{1}{2}\left[\frac{d^2\sigma_{\rm mag}}{d\omega\,d\Omega}\right]=\left[\frac{d^2\sigma^{(+-)}}{d\omega\,d\Omega}\right]_{\rm HF}-\left[\frac{d^2\sigma^{(+-)}}{d\omega\,d\Omega}\right]_{\rm VF}\ . \tag{2}$$

The paramagnetic scattering function is expressed as

$$S(q,\omega)=M^2(q)\frac{\hbar\omega/kT}{1-\exp(-\hbar\omega/kT)}\frac{1}{\pi}\frac{\Gamma}{\Gamma^2+\omega^2}\ , \tag{3}$$

where $M^2(q)$ is written as

$$M^2(q)=M^2(0)\frac{\kappa_1^2}{\kappa_1^2+q^2}\ . \tag{4}$$

The magnetic scattering has been observed around the (1,1,0) and (1,1,1) reciprocal-lattice points as shown in Fig. 2. The data are obtained with the analyzer set at $\Delta E=0$ of 41 meV neutrons. The intensity is higher around the (1,1,0) than around the (1,1,1) point, which is consistent with the difference of the product $f^2(Q)F_M^2$ at the two reciprocal-lattice points, where F_M^2 is the structure factor assuming ferromagnetic ordering of Fe. No appreciable magnetic scattering has been observed around the (2,0,0) point, where F_M^2 is calculated to be negligible. The calculated values of F_M^2 assuming ferromagnetic structure are listed in Table I.

TABLE I. The magnetic structure factor F_M^2 of FeSi calculated by assuming ferromagnetic ordering of the Fe atoms.

Index	F_M^2
1,0,0	0
1,1,0	0.93
1,1,1	1
2,0,0	0.07

The constant Q scan has been performed along the [110] direction around the (1,1,0) reciprocal-lattice point in the temperature range between 150 and 600 K. Spectra for various ζ (reduced q) at 300 and 500 K are shown in Figs. 3 and 4. The shape of the spectrum is very sharp at small value of ζ while it becomes broad at larger ζ. However, the integration of the spectrum over energy has been found to be independent of ζ as illustrated for various temperatures in Fig. 5. These integrated values are normalized by $f(Q)^2$. Nontrivial decrease of the integrated intensity at large ζ, which appeared at lower temperature as 300 K, is due to incomplete integration of the spectrum, because Γ becomes very large and the constant q scan could not cover the full energy range of the spectrum. The results of Fig. 5 make a contrast with those in Fig. 2 where the measurement was made with

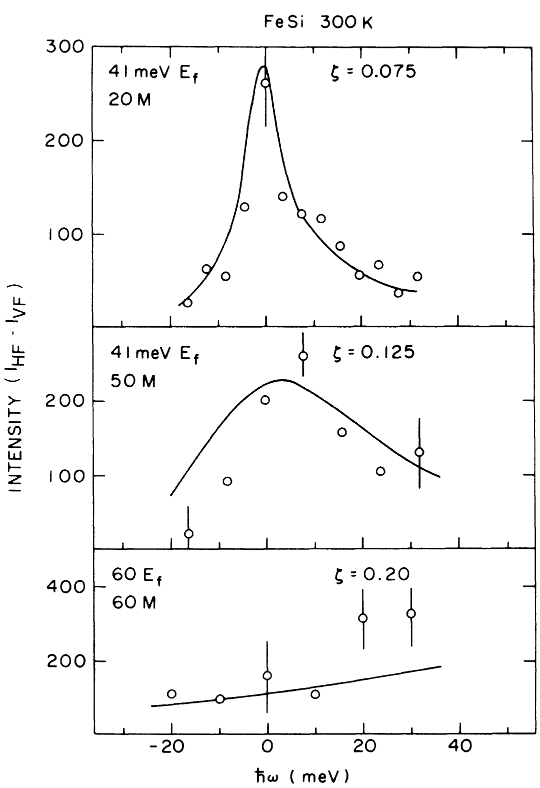

FIG. 3. Constant q spectra taken with the $I_{\rm HF}-I_{\rm VF}$ mode at 300 K. Solid lines are the result of fitting calculation using Eq. (3) (see text). $10M$ corresponds approximately 10 min counting time at $\hbar\omega=0$.

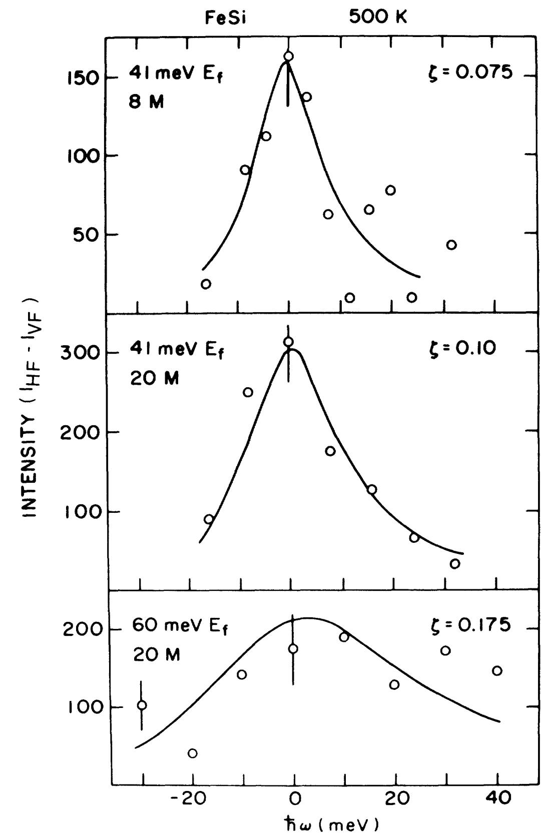

FIG. 4. Constant q spectra taken with the $I_{\rm HF}-I_{\rm VF}$ mode at 500 K. Solid lines are the result of fitting calculation using Eq. (3) (see text). $10M$ corresponds approximately to 10 min counting time at $\hbar\omega=0$.

the analyzer set at $\Delta E=0$, and indicate that there is no instantaneous ferromagnetic correlation. Therefore, the analysis using Eqs. (3) and (4) has been made by assuming the inverse correlation range κ_1 to be infinity. Solid lines in Figs. 3 and 4 are results of the convolution of the Eq. (3) with the resolution function of the spectrometer. M^2 in Eq. (3) is held fixed for a given T, consistent with $\kappa_1 \rightarrow \infty$. The only parameter for the fitting of the spectrum is Γ and the good agreement between calculations and observations is obtained with this assumption.

Since the origin of the anomalous paramagnetism in FeSi is due to the unique band structure as shown in the inset of Fig. 1, we expected to observe two contributions to the total scattering function,

$$S(q,\omega)=[S(q,\omega)]_{\rm para}+[S(q,\omega)]_{\rm gap}\ , \tag{5}$$

where $[S(q,\omega)]_{\rm para}$ is a general paramagnetic function of Eq. (3) and $[S(q,\omega)]_{\rm gap}$ is the magnetic scattering function which reflects the band gap model. The latter may be expected to be an illustration of Fig. 6. As the band gap 2Δ is estimated to be ~ 50 meV,[22] we might observe a spectrum of which the peak position deviates appreciably from $E=0$. Such a deviation has appeared in a spectrum at $\zeta=0.2$ in Fig. 3. However, we could not distinguish

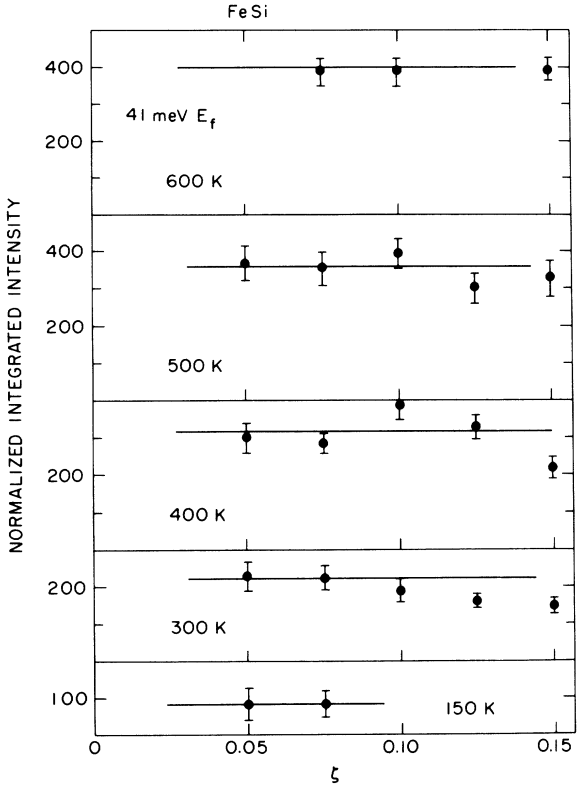

FIG. 5. The integrated intensity of the constant q data for various ζ and temperatures. These values are normalized by $f(Q)^2$.

contributions from $[S(q,\omega)]_{para}$ and $[S(q,\omega)]_{gap}$ in the present measurement because the deviation of the peak position in $[S(q,\omega)]_{para}$ is also large if $\Gamma > kT$. A solid line in the spectrum of $\zeta=0.2$ in Fig. 3 has been obtained using only $[S(q,\omega)]_{para}$ with $\Gamma=60$ meV. In this analysis, we have only used $[S(q,\omega)]_{para}$ for all spectra.

M^2 can be expressed by the integration of $S(q,\omega)$ over energy through the relation,

$$M^2=6\int_{-\infty}^{+\infty} S(q,\omega)d\omega \ . \tag{6}$$

The integrated intensity at various temperatures in Fig. 5 which is indicated by solid lines thus corresponds to M^2 and is plotted against temperature in Fig. 7 (open circles). M^2 obtained from the fitting of Eq. (3) with constant Q data, which is described above, are also shown by solid circles. A solid line is the result of the calculation $M^2(0)=3kT\chi(0)$ using the static susceptibility.[1] The absolute value of the integrated intensity was determined from the phonon intensity measurement[8] of the same sample. M^2 at 300 K was determined to be $(3.5\pm2)\mu_B^2$ which agrees with $3kT\chi(0)$ at the same temperature within experimental error. Thus, the temperature dependence of the M^2 determined from the neutron scattering and the susceptibility measurement are in agreement with each other.

The q dependence of Γ at various temperatures obtained from the analysis is illustrated in Fig. 8. It exhibits a unique feature in FeSi. At 300 K, the q dependence is very steep while it becomes moderate at high temperatures. The constant q spectrum at large ζ becomes sharp at high temperatures as compared in Fig. 9 in the case of $\zeta=0.15$. On the other hand, in the small ζ region, the width of the high-temperature spectrum is broader than at low temperature. The temperature dependence of Γ at $\zeta=0.15$ and 0.075 are compared in Fig. 10.

It should be mentioned to the difficulty of the measurement of the magnetic scattering from FeSi. As mentioned above, the absolute value of M^2 was determined to be $(3.5\pm2)\mu_B^2$ at 300 K. The value is twice as large at 600 K, but it should be emphasized that it almost corresponds to the smallest value of the observation for $M^2(q,T)$ measured in Fe (Ref. 18) and Ni (Ref. 19) and is constant throughout the Brillouin zone. The strong q dependence of the linewidth, especially at low temperature with small M^2, makes the observation of magnetic scattering at large q almost impossible. Many attempts

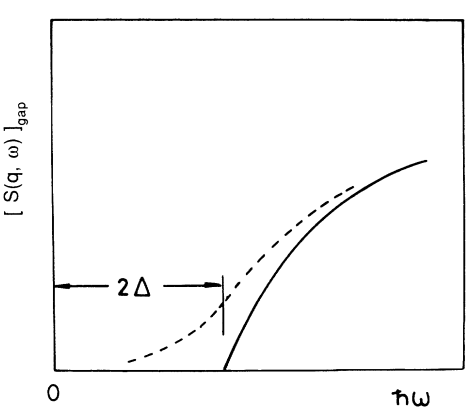

FIG. 6. The schematic diagram for the scattering cross section $[S(q,\omega)]_{gap}$ caused by the interband transition. The dotted line is $[S(q,\omega)]_{gap}$ at finite temperatures. 2Δ is the band gap shown in the inset of Fig. 1 (after the private communication from Y. Takahashi).

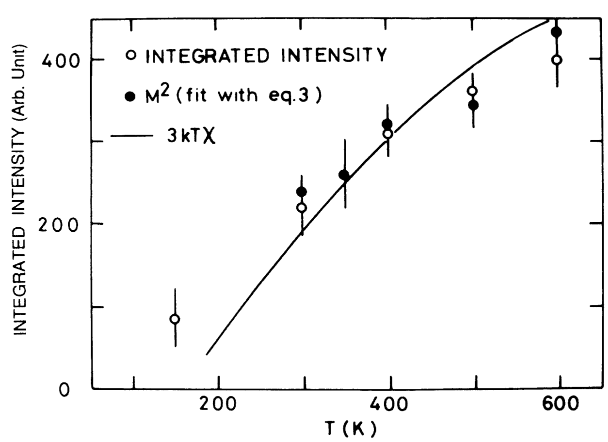

FIG. 7. The temperature variation of the integrated intensity of constant-q spectra (open circles). M^2 determined from the Lorentzian fitting analysis using Eq. (3) is also plotted (solid circles). The solid line represents $3kT\chi(0)$ calculated using the data shown in Fig. 1.

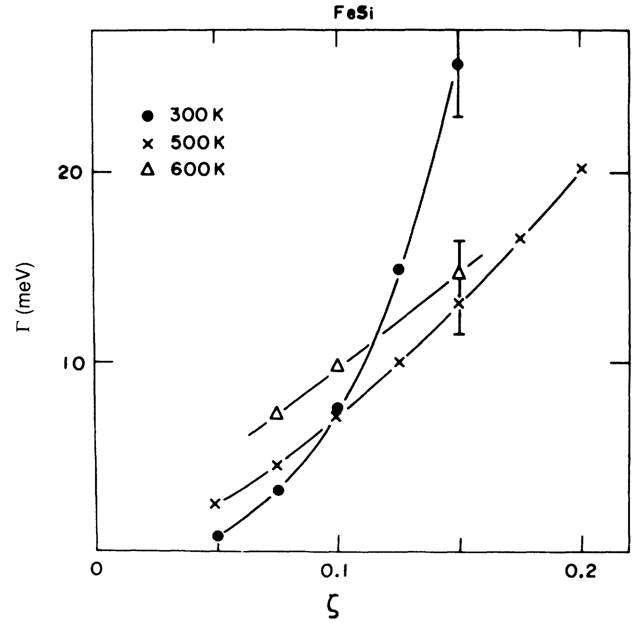

FIG. 8. The q dependence of the inverse lifetime Γ at various temperatures. Solid lines are the fitting curve $\Gamma = Aq^{\alpha}$ with $A = 1000$ meV A^{-3} and $\alpha = 3$ at 300 K, $A = 82$ meV $A^{-1.5}$, and $\alpha = 1.5$ at 500 K and $A = 50$ meV A^{-1} and $\alpha = 1$ at 600 K, respectively.

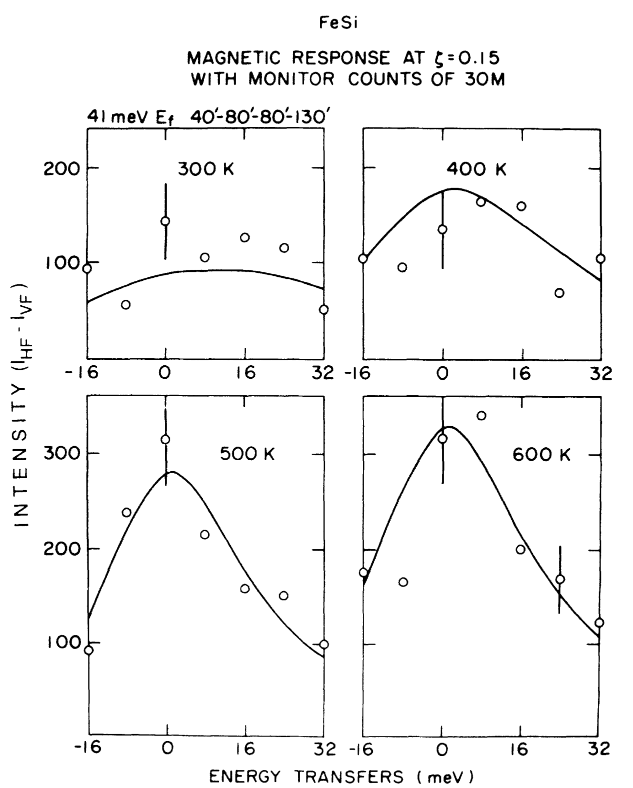

FIG. 9. The comparison of the constant q spectrum of $\zeta = 0.15$ at various temperatures. Solid lines are the calculated fitting curve using Eq. (3).

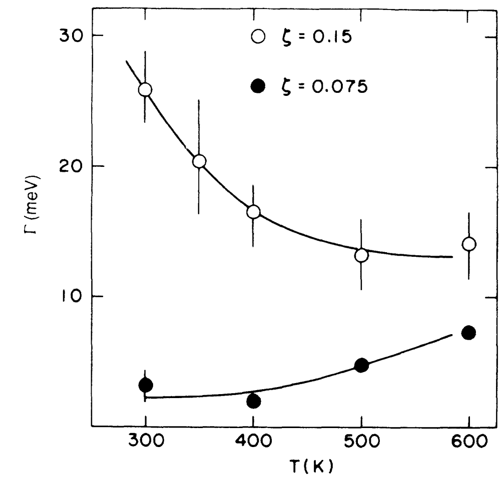

FIG. 10. The temperature dependence of Γ at $\zeta = 0.15$ (open circles) and $\zeta = 0.075$ (solid circles). Solid lines are the guide for the eye.

have been made to overcome such severe experimental conditions, and we finally settled on a rather coarse resolution in order to obtain sufficient intensity. The observation of the magnetic signal with $\zeta > 0.2$ was still very difficult. The measurement with better resolution, e.g., 13.7 meV, near the zone center is not successful because of no enhancement of the scattering intensity as in Fe and Ni. The comparison of the magnetic intensity with that of phonons is demonstrated in Fig. 11. The longitudinal phonon with $\zeta = 0.15$ has been measured with the spin nonflip mode using $E_f = 30$ meV. The magnetic intensity which is illustrated as the shaded part in the figure are the estimation from the measurement at $\zeta = 0.05$. The ratio of the magnetic intensity to nuclear one is very small, therefore, the mixing of the nuclear scattering to

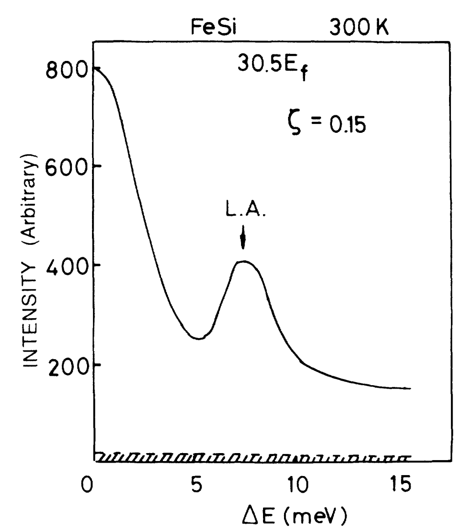

FIG. 11. The comparison of the intensities of the nuclear (solid line) and magnetic (shaded) scattering of $\zeta = 0.15$ at 300 K (see text).

the magnetic intensity, which is caused by the difference of the spin flipping ratio between VF and HF modes, are checked frequently and confirmed to be negligible. It is now clear why previous experiments by Motoya *et al.*[10] and Kohgi and Ishikawa[11] could not detect the magnetic signal. The former made the experiment on a powdered sample with a polarized neutron beam, but the intensity of the incident neutron is not supposed to be sufficient to detect the magnetic signal. Using the unpolarized beam, the latter concentrated the experiment at large ζ (~ 0.5) because the phonon spectrum prevents observation of the magnetic signal in the small ζ region. As has been mentioned above, it is almost impossible to detect the magnetic scattering at $\zeta \sim 0.5$ even in the High Flux Beam Reactor.

III. DISCUSSION

As was shown in Fig. 7, direct observation of the temperature-induced magnetic moment in FeSi has succeeded with the polarized neutron technique. The results are in good agreement with the calculation from the static susceptibility measurement. We believe that this is concrete evidence for the model of the temperature induced paramagnetism in FeSi. The integrated intensity or M^2 observed in the measured temperature range does not depend on q, i.e., there is no instantaneous correlation between magnetic moments. However, as shown in Figs. 2 and 8, the magnetic scattering has been observed only around the "ferromagnetic" reciprocal-lattice points and the inverse life time Γ of the spin fluctuation tends to vanish as $q \rightarrow 0$. Therefore, the spin fluctuations with small q dominate if we take the long time average, and it is clear that the exchange interaction in FeSi is *ferromagnetic*. The similar behavior of M^2 and Γ in spin fluctuation was also observed[23] in the localized spin ferromagnet Pd_2MnSn well above the Curie temperature ($T = 4T_c$).

The temperature dependence of $\Gamma(q)$ is remarkable and this is the unique feature in FeSi. The power of q in Γ varies from q^3 at 300 K to q^1 at 600 K. The theoretical descriptions of Γ are given for metals and alloys,[24] but these theories are only for weak ferromagnets and metals such as Fe and Ni, and cannot be applied to the present experimental results. The paramagnetic moment M^2 in FeSi is thought to appear with the thermally excited electrons in the conduction band and holes in the valence band, and $[S(q,\omega)]_{\mathrm{para}}$ includes informations of these band transitions. Therefore, the dynamics of the magnetic moment, i.e., Γ of the spin fluctuation is controlled by the relaxation process of interband and/or intraband transitions which may give an appreciable temperature dependence reflecting the temperature dependence of the Fermi distribution function. Although Γ increases slightly with increasing temperature at small ζ region, it decreases dramatically in the large ζ region, as is shown in Figs. 8 or 10. Constant q spectra of $\zeta = 0.15$ at various temperatures demonstrate the dramatic decrease of Γ, as is shown in Fig. 9. In general, Γ exhibits smaller value in the localized spin system than in the itinerant-spin system, as has been summarized by Shirane *et al.*[25] According to Takahashi and Moriya,[4] the magnetic moment in FeSi is induced thermally through the negative mode-mode coupling of the spin fluctuations, and at high temperature, this temperature-induced magnetic moment saturates and behaves as the localized magnetic moment. Therefore, it is speculated that the small value of Γ at high temperature in FeSi reflects the localized character of the magnetic moment which is also consistent with the model of the temperature-induced paramagnetism proposed by Moriya.[26]

As has been pointed out by Ishikawa *et al.*[8] on the experiment with MnSi, it is quite important to estimate the contribution of the *zero-point* spin fluctuation to the observed spectrum. In order to evaluate the pure *thermal* spin fluctuation, Ishikawa *et al.*[8] proposed that the integration of the constant Q spectrum should be made only in the region of negative energy (neutron energy gain) side. In the present experiment of FeSi, measuring temperatures are rather high compared with that of MnSi and q is restricted to a small range. Therefore, the contribution from the zero-point spin fluctuation is small and within an experimental error. However, if we extend the measurement to low-temperature and/or large-q region where the spectrum of the spin fluctuation spread to higher energy transfer, the contribution of the zero-point spin fluctuation becomes appreciably large compared with that of the temperature-induced spin fluctuation.

Present experimental results are analyzed only based on the simple Lorentzian scattering cross section of Eq. (3). As mentioned in the preceding section, the estimation of the contribution from $[S(q,\omega)]_{\mathrm{gap}}$ is very difficult and we have omitted this term. Both the temperature dependence and the absolute value of M^2 obtained from the present analysis are consistent with the calculation using static susceptibility, which suggest, from the sum rule of the scattering intensity, that there is no contribution from $[S(q,\omega)]_{\mathrm{gap}}$. However, because of the difficulty of the experiment, the accuracy of the experiment may be not enough to give a definitive conclusion on this point and it may be worth it to proceed with the experiment using higher energy and higher flux neutrons.

The magnetic scattering from the anomalous paramagnet FeSi has been observed and results seem to be described rather well by the model of the temperature-induced paramagnetism. However, in order to understand the behavior of FeSi in more detail and quantitatively, especially for $\Gamma(q,T)$, we should wait for the detailed calculation based on the actual band structure.

ACKNOWLEDGMENTS

This work was carried out as part of the U.S.-Japan cooperative neutron scattering program. The authors would like to thank T. Moriya and Y. Takahashi for theoretical discussions, P. Böni, A. Goldman, M. Kohgi, S. Mitsuda, N. Wakabayashi, and Y. Yamada for valuable discussions and M. Onodera and T. Miura for providing the single crystal. One of the authors (K.T.) appreciated the kind hospitality of the members of the neutron scattering group at Brookhaven National Laboratory while he was working there. Work at Brookhaven is supported by the U.S. Department of Energy under Contract No. DE-AC02-76CH00016. Work at Tohoku University was supported by the Grant-in-Aid for Scientific Research from Japanese Ministry of Education, Science and Culture.

---

*On leave from the University of Pennsylvania, Philadelphia, PA 19104.

[1]V. Jaccarino, G. K Wertheim, J. H. Wernick, and L. R. Walker, Phys. Rev. **160**, 476 (1967).

[2]H. Watanabe, H. Yamamoto, and K. Ito, J. Phys. Soc. Jpn. **18**, 995 (1963).

[3]O. Nakanishi, A. Yanase, and A. Hasegawa, J. Magn. Magn. Mater. **15-18**, 879 (1980).

[4]Y. Takahashi and T. Moriya, J. Phys. Soc. Jpn. **46**, 1451 (1979).

[5]For example, T. Moriya, *Spin Fluctuations in Itinerant Electron Magnetism* (Springer-Verlag, Berlin, 1985).

[6]Y. Takahashi, M. Tano, and T. Moriya, J. Magn. Magn. Mater. **31-34**, 329 (1983).

[7]S. N. Evangelou and D. M. Edwards, J. Phys. C **16**, 2121 (1983).

[8]Y. Ishikawa, Y. Noda, Y. J. Uemura, C. F. Majkrzak, and G. Shirane, Phys. Rev. B **31**, 5884 (1985).

[9]K. Adachi, K. Sato, and M. Takeda, J. Phys. Soc. Jpn. **26**, 631 (1969).

[10]K. Motoya, M. Nishi, and Y. Ito, J. Phys. Soc. Jpn. **49**, 1931 (1980).

[11]M. Kohgi and Y. Ishikawa, Solid State Commun. **37**, 833 (1981).

[12]K. R. A. Ziebeck, H. Capellman, P. J. Brown, and P. J. Webster, J. Magn. Magn. Mater. **36**, 160 (1983).

[13]S. J. Oh, J. W. Allen, and J. M. Lawrence, Phys. Rev. B **35**, 2267 (1987).

[14]R. M. Moon, T. Riste, and W. C. Koehler, Phys. Rev. **181**, 920 (1969).

[15]K. R. A. Ziebeck and P. J. Brown, J. Phys. F **10**, 2015 (1980).

[16]J. P. Wicksted, P. Böni, and G. Shirane, Phys. Rev. B **30**, 3655 (1984).

[17]Y. J. Uemura, G. Shirane, O. Steinsvoll, and J. Wicksted, Phys. Rev. Lett. **51**, 2322 (1983).

[18]G. Shirane, P. Böni, and J. Wicksted, Phys. Rev. B **33**, 1881 (1986), and references therein.

[19]J. Martinez, P. Böni, and G. Shirane, Phys. Rev. B **32**, 7037 (1985), and references therein.

[20]K. Tajima, P. Böni, G. Shirane, Y. Ishikawa, and M. Kohgi, Phys. Rev. B **35**, 274 (1987).

[21]G. Shirane, J. E. Fischer, Y. Endoh, and K. Tajima, Phys. Rev. Lett. **59**, 351 (1987).

[22]R. Wolfe, J. H. Wernick, and S. E. Haszko, Phys. Lett. **19**, 449 (1965).

[23]M. Kohgi, Y. Endoh, Y. Ishikawa, H. Yoshizawa, and G. Shirane, Phys. Rev. B **34**, 1762 (1986).

[24]For example, Y. Takahashi, J. Phys. Soc. Jpn. **55**, 2390 (1986).

[25]G. Shirane, Y. J. Uemura, J. P. Wicksted, Y. Endoh, and Y. Ishikawa, Phys. Rev. B **31**, 1227 (1985).

[26]T. Moriya, J. Phys. Soc. Jpn. **45**, 397 (1978).