

Mössbauer spectroscopy and magnetic transition of λ -(BETS)₂FeCl₄

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The compound λ -(BETS)₂FeCl₄ provides an effective demonstration of the interaction of π conduction electron and d -electron localized moment systems in molecular crystalline materials where antiferromagnetic insulating and magnetic field induced superconducting states can be realized. The metal-insulator transition has been thought to be cooperative, involving both the itinerant π -electron and localized d -electron spins where antiferromagnetic order appears in both systems simultaneously. However, recent specific-heat data has indicated otherwise [H. Akiba, S. Nakano, Y. Nishio, K. Kajita, B. Zhou, A. Kobayashi, and H. Kobayashi, J. Phys. Soc. Jpn. **78**, 033601 (2009)]; although the π -electron system orders antiferromagnetically and produces a metal-insulator transition, a paramagnetic d -electron state remains. We report ⁵⁷Fe Mössbauer measurements that support the paramagnetic model provided the d -electron spins remain in a fast relaxation state below the transition. From the measured hyperfine fields, we also determine the temperature dependence of the π - d electron exchange field.

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λ -(BETS)₂FeCl₄ (BETS=bisethylenedithio-tetraselenafulvalene) is one of the most thoroughly studied molecular conductors in the last few years due to its unique properties derived from the interaction between conducting π electrons in the BETS donor layers and localized d -electrons in FeCl₄ anions with $S=5/2$ spins.¹ The crystal structure² of λ -(BETS)₂FeCl₄ as shown in Fig. 1 consists in stacks of BETS donors along a and tightly packed in layers with a two-dimensional (2D) network of $S\dots S$ contacts parallel to (a, c) , alternating along b with layers of FeCl₄ anions. At high temperatures this compound is a quasi-2D metal due to delocalization of π -electrons in the layered network of partially oxidized donors, and its magnetic susceptibility is dominated by the paramagnetic $S=5/2$ FeCl₄ spins. At 8.3 K this compound undergoes a transition toward an antiferromagnetic (AF) insulating ground state (see inset of Fig. 3 below). Since the isomorphous compound with diamagnetic GaCl₄ anions remains metallic, becoming superconductor at 6 K, the metal-insulator transition in λ -(BETS)₂FeCl₄ has been thought to be driven by the ordering of the Fe spins.

However until now no direct microscopic measurements directly probing the role of the anions have been published and recent specific-heat measurements by Akiba *et al.* cast some doubts on the role of the $S=5/2$ FeCl₄ spins in the transition.³ These authors have suggested that during the transition, while the π spins order antiferromagnetically, the Fe spins remain paramagnetic below 8.3 K. According to their model an effective field $H_{\pi-d} \approx 4$ T caused by the ordering of the π spin system is switched on at the Fe sites at approximately 8.3 K but the Fe³⁺ cations remain paramagnetic with the 3d energy levels described by a Zeeman splitting. The latter gives rise to a Schottky six-level term in the specific heat, and the computed entropy clearly shows that the main contribution to both the specific heat jump at 8.3 K and at lower temperatures is due to the spin 5/2 system (i.e., Rln6).

In this Rapid Communication we describe the results of a ⁵⁷Fe Mössbauer spectroscopy study to examine the role of the Fe $S=5/2$ spins in the transition. The single crystals of λ -(BETS)₂FeCl₄ used in this work were grown using standard electrochemical methods from 99% ⁵⁷Fe enriched TEAFeCl₄. Mössbauer spectra were collected with the absorber within a liquid-He bath cryostat, in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi ⁵⁷Co source in a Rh matrix. The absorber was prepared by randomly placing between two perspex plates approximately 4 mg of λ -(BETS)₂FeCl₄ single crystals 99% enriched in ⁵⁷Fe. Electrical transport measurements, which verified the metal-insulator transition in the ⁵⁷Fe enriched samples at $T_N=8.3$ K (inset of Fig. 3), were carried out us-

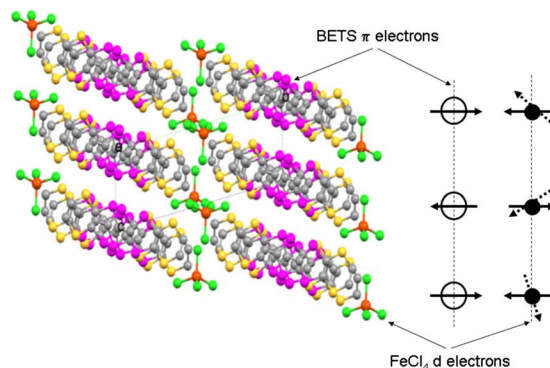


FIG. 1. (Color online) Crystal structure of λ -(BETS)₂FeCl₄ projected in the b - c plane (drawn after the crystal data from Ref. 2). The charge transfer of one electron between each two BETS donors and one FeCl₄ anion leaves a delocalized spin 1/2 π electron on the donor stacks, and a localized d -electron at the anion site. The schematic shows the two possible spin configurations below T_N with fully antiferromagnetic π and d order (solid arrows) or with a paramagnetic d state (dashed arrows).

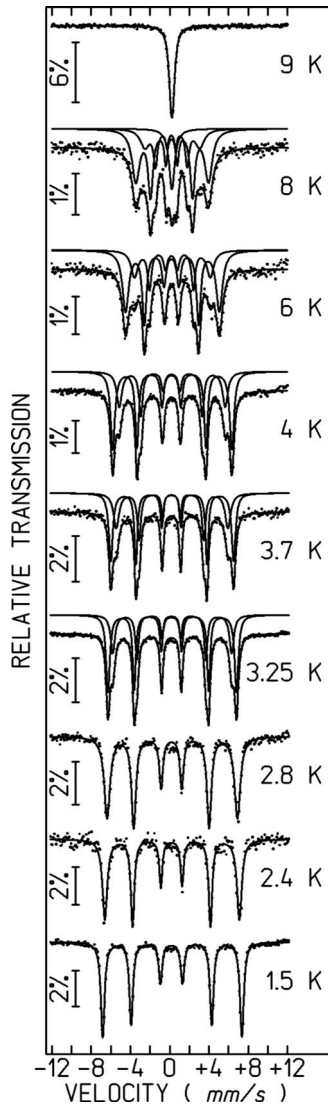


FIG. 2. ^{57}Fe Mössbauer spectra of $\lambda\text{-(BETS)}_2\text{FeCl}_4$ for different temperatures. The individual solid lines are components of the spectrum coming from the two sextets and quadrupole components. The solid line through the data (dots) is the sum of the individual contributions.

ing a standard four-terminal resistance configuration on crystals that had been used in the Mössbauer measurements.

Mössbauer spectra obtained at different temperatures in the range 9–1.5 K are shown in Fig. 2, and the fitting parameters are listed in Table I. The spectra were fitted to Lorentzian lines using a nonlinear least-squares method.⁴ The relative areas and linewidths of both peaks in a quadrupole doublet and the peak pairs 1–6, 2–5, and 3–4 in a magnetic sextet were constrained to remain equal during the refinement procedure. Isomer shifts (ISs) are given relative to $\alpha\text{-Fe}$ at room temperature. Above 8.3 K the spectra present a single line typical of paramagnetic Fe^{3+} in a site with a low quadrupole distortion (high-symmetry environment). Below 8.3 K sextet splittings are observed. The spectrum obtained at 8 K still shows a small fraction (approximately 13%) of “paramagnetic” atoms, which can be ascribed to a hysteresis or the slow dynamics of the transition. Below this tempera-

TABLE I. Computed parameters from the Mössbauer spectra of $\lambda\text{-(BETS)}_2\text{FeCl}_4$ taken at different temperatures. IS, isomer shift relative to metallic Fe at 298 K. Quadrupole splitting (QS). $\epsilon = (e^2V_{ZZ}Q/4)(3\cos^2\theta - 1)$, quadrupole shift. B_{hf} , magnetic hyperfine field. Γ , half-width of the doublet peaks. I , relative area. Estimated errors: ≤ 0.02 mm/s for IS, QS, ϵ , Γ ; ≤ 0.2 T for B_{hf} .

T (K)	IS (mm/s)	QS, ϵ (mm/s)	B_{hf} (T)	Γ (mm/s)	I (%)
200	0.27	0.21		0.49	100
9.0	0.34	0.20		0.54	100
8.0	0.34	0.20		0.57	13 \pm 2
	0.33	0.10	17.3	0.33	26 \pm 4
	0.33	0.07	22.9	0.40	61 \pm 4
7.2	0.34	0.11	20.1	0.41	32 \pm 3
	0.34	0.08	26.0	0.39	68 \pm 3
6.1	0.34	0.10	23.9	0.47	32 \pm 2
	0.34	0.10	29.6	0.52	68 \pm 2
4.1	0.34	0.08	33.5	0.43	36 \pm 1
	0.34	0.09	37.6	0.42	64 \pm 1
3.7	0.34	0.07	35.3	0.29	43 \pm 3
	0.34	0.08	38.8	0.33	57 \pm 3
3.25	0.33	0.08	37.6	0.32	38 \pm 1
	0.33	0.08	40.6	0.36	62 \pm 1
2.8	0.33	0.09	41.2	0.45	100
2.4	0.33	0.07	42.5	0.38	100
1.8	0.34	0.09	43.7	0.61	100
1.5	0.34	0.09	44.0	0.44	100

ture, down to 3.2 K, two magnetic splittings are clearly seen. They have identical isomer shifts but slightly different hyperfine fields, B_{hf} . This clearly indicates that there are two different magnetic environments for the Fe sites. The uncertainty in the relative areas of the sextets is relatively large, but in a first approximation they present a temperature independent 1:2 ratio. Below 3 K, these two sextets appear to merge and only one sextet is observed in the range 2.8–1.5 K. This effect may result from different temperature dependencies of the magnetic hyperfine fields of both sextets. The less intense subspectrum would overlap the dominant one around 3 K. This interpretation is supported by the fact that if only one sextet is used to fit the spectra below 3 K, an increase in peak width is observed (Table I) and the estimated B_{hf} seems to be an average of both B_{hf} above 3 K, extrapolated to lower temperatures (Fig. 3). Another possible explanation would be a transition occurring at 3.0 ± 0.1 K. Changes below T_N have indeed been seen in other independent studies in the 3 K region. Matsui and co-workers⁵ investigated the microwave cavity response with $\lambda\text{-(BETS)}_2\text{FeCl}_4$, and below T_N have found highly dispersive modes attributed to charge degrees of freedom. However, for $H_{ac} \parallel H \parallel a^*$, a peak in the cavity dissipation ($\Delta\Gamma/2f_0$) appears at 3 K ($H=0$) which, due to the unfavorable direction of the eddy currents for $H_{ac} \parallel a^*$, the authors attribute to a dynamic response due to spin degrees of freedom. This peak has a complicated dependence on H near the 1.2 T spin-flop tran-

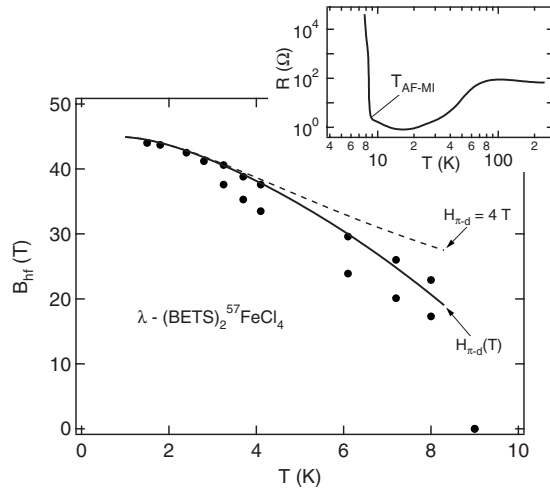


FIG. 3. Temperature dependence of the Fe hyperfine fields, B_{hf} in λ -(BETS) $_2$ FeCl $_4$. The lines represent the fast relaxation model for both fixed and temperature-dependent $H_{\pi-d}$ exchange fields (see text). Inset: temperature-dependent resistance of a single crystal of 57 Fe enriched λ -(BETS) $_2$ FeCl $_4$ showing the M - I transition at 8.3 K.

sition. Likewise, Rutel *et al.*⁶ observed anomalies in the microwave cavity response below 4 K for $H\parallel c$.

The hyperfine fields B_{hf} shown in Fig. 3, present significant temperature dependence until approximately 3 K. Below this temperature they seem to saturate approaching 44 T at 1.5 K, very close to the value of $B_{hf}=45$ T observed for FeCl $_3$ at 4.2 K.⁷

The observed change in the shape of the Mössbauer spectra in a narrow temperature range around 8.3 K is indicative of a magnetic ordering process. Clearly, above the M - I transition the Fe $^{3+}$ spins are oscillating with a relaxation frequency $\omega_R > 10^{12}$ Hz, typical of paramagnetic Fe $^{3+}$. In this situation the magnetic field observed at the Fe nuclei is averaged to zero.^{7,8} In a first approximation the presence of sextets with sharp peaks as those observed below the M - I transition suggests that the Fe nuclei are feeling a static magnetic hyperfine field within the observation time scale of the Mössbauer effect. This would imply that the relaxation frequency of the Fe $^{3+}$ spins is now $\omega_R < 10^8$ Hz.

The abrupt change in ω_R in a narrow temperature range is typical of the establishment of long-range magnetic correlations, namely, of magnetic ordering, of the Fe sublattice. This would not agree with the interpretation of the specific-heat data.³ However an alternative analysis of the present Mössbauer data may explain equally well the observed spectra. In the proposed picture of Akiba *et al.*³ based on specific-heat data of λ -(BETS) $_2$ FeCl $_4$, the Fe $S=5/2$ spins remain paramagnetic below the transition at 8.3 K although subject to an internal effective field $H_{\pi-d} \sim 4$ T switched on at the Fe sites by the ordering of the π spin system. In the absence of $H_{\pi-d}$, if the Fe atoms remain in the paramagnetic state in a fast relaxation regime, the magnetic field in the nuclei averages to zero and only a two-line pattern should appear corresponding to the electric quadrupole interaction (in this case a single absorption peak is observed due to the very low quadrupole splitting), evident at 9 K. If there was a drastic slowing down of the electronic relaxation, but in the absence

of magnetic ordering, two different sextets should be observed, corresponding to the different M_S states 5/2, and 3/2, as it has been observed in diluted 57 Fe doped compounds, such as in Fe-doped Al $_2$ O $_3$,⁹ LiAl $_5$ O $_8$,¹⁰ or in proteins such as the transferrins.¹¹ The $M_S=1/2$ state should result in a complicated 11-line pattern since it induces nondiagonal terms in the Hamiltonian of the hyperfine interactions.¹² Although its presence was reported in the transferrin case¹¹ it usually is not observed due to enhanced relaxation of the $M_S = \pm 1/2$ electronic doublet.⁹

Unlike dilute systems, the concentration of Fe $^{3+}$ in λ -(BETS) $_2$ FeCl $_4$ is not so low as in the above examples and therefore due to spin-spin interactions a slow relaxation regime is not expected to occur. It could be argued that in λ -(BETS) $_2$ FeCl $_4$ the internal effective field of the donors at the Fe sites, estimated as $H_{\pi-d} \sim 4$ T, could freeze the spin flipping and bring the system to a slow relaxation regime. However there is no evidence for the $M_S=3/2$ state. The sextet with the smaller magnetic splitting observed between 8 and 3 K cannot correspond to the $M_S=3/2$ state because its B_{hf} value is $\geq 90\%$ of the B_{hf} of the larger magnetic splitting (below 4.1 K where thermal excitations are less important). The saturated B_{hf} values associated with $M_S=3/2$ and 5/2 electronic states should be proportional to M_S .¹¹ Furthermore in such case the relative intensities of both magnetic splittings should follow the evolution of their statistical thermal population,¹² while they remain approximately constant.

As shown, in the absence of a magnetic field, a paramagnetic state both in the slow and fast relaxation limits does not fit the present spectra. It is however difficult for a Mössbauer probe to discriminate between the onset of magnetic order, spin-glass, behavior, or a particular case of a paramagnetic “fast relaxation” behavior where the Fe spins are Zeeman split by an applied field and the population of M_S states are different. The present results may therefore be consistent with the Fe atoms remaining paramagnetic in the low temperature state below 8.3 K. Assuming a fast relaxation model below the transition, we may compute the hyperfine field B_{hf} based on the Fe nuclei, induced by a Zeeman splitting and a Boltzmann distribution of the six M_S electronic states:

$$B_{hf}(T) = \sum_{M_S} [B(M_S) \exp(X_{M_S})] / \sum_{M_S} \exp(X_{M_S}). \quad (1)$$

Here $X_{M_S} = -g\mu_B M_S H_{\pi-d} / k_B T$. We take $B(M_S) \sim \pm 45$ T for $M_S = \mp 5/2$, ± 27 T for $M_S = \mp 3/2$, and ± 9 T for $M_S = \mp 1/2$ (in proportion to M_S). In Fig. 3 the computed temperature dependence of B_{hf} is shown for both a constant $H_{\pi-d}=4$ T, and for a temperature dependent $H_{\pi-d}$, increasing from 2.45 T at 8 K to 4.2 T at 1.5 K. We find that the best fit to the data implies that $H_{\pi-d}$ is temperature dependent. Although this modifies the temperature dependence of the Schottky specific heat described by Akiba *et al.*,³ the differences are not significant.

The temperature dependence of the exchange field may be described by a spin-wave behavior^{13,14} where, for antiferromagnetic dispersion in the spin 1/2 π -electron system $\omega = J/\hbar |ka|$ (k as the wave vector and a as the lattice constant), $H_{\pi-d}(T) = H_{\pi-d}(0)(1 - AT^3)$. We find that for $A \sim 7 \times 10^{-4}$ K $^{-3}$, Eq. (1) provides a reasonable description of the

temperature dependence of B_{Hf} , shown as the solid line in Fig. 3. From A we estimate the spin-wave exchange energy to be $J \sim 5.6$ K, comparable to T_N .

The suggestion and evidence that the magnetic order appears in the π -electron system but not in the d -electron system, seems unusual.¹⁵ However, estimates do show that the mean-field exchange interaction of the π -electron system is the largest: $J_{\pi-\pi}$, $J_{\pi-d}$, and J_{d-d} are 448, 14.6, and 0.64 K, respectively.¹⁶ Nevertheless, the d -electron spins must play a central role in the formation of the magnetic ground state. A temporal probe of the spin dynamics of the d -electron system below the $M-I$ transition, as well as magnetic-field-dependent specific heat and Mössbauer experiments, would

be useful to further explore the nature of the magnetic order associated with this very unusual antiferromagnetic metal-insulator transition.

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