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One-dimensional antiferromagnetic coupling in the low-carrier heavy-electron system Yb_4As_3: The role of charge ordering

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Inelastic-neutron-scattering experiments on Yb_4As_3 revealed the existence of low-energy spin excitations, which are characteristic of a one-dimensional Heisenberg-type antiferromagnetic coupling at low temperatures where charge ordering takes place. Superimposed on the one-dimensional spin excitations, an unusual magnetic response is also observed around the one-dimensional zone center. These results strongly suggest that the heavy-electron behavior in Yb_4As_3 is a unique phenomenon caused by charge ordering; it results from the fact that the compound contains doped one-dimensional $4f^1$ hole chains with strong on-site f-electron correlations. [S0163-1829(97)50642-4]

In the past two decades, a rich variety of unusual phenomena related to heavy-electron properties was found.[1] Most of these phenomena are attributed to a common origin in which hybridization of f orbits and conduction electrons gives rise to complete screening of the magnetic moment of localized f electrons by the conduction-electron spins (the Kondo effect) and make f electrons itinerant with a heavy mass at low temperatures. Recently, a new class of anomalous phenomena was found in some Ce or Yb compounds, such as CeX (X=P,As,Sb,Bi), YbX (X=N,P,As), or another pnictide compound, Yb_4As_3.[2] These compounds show not only anomalous magnetic properties but also the phenomena that are typically seen in the dense-Kondo heavy-electron systems in spite of the very small carrier density in these compounds: typically on the order of 10^{-3}–10^{-2} carriers per formula unit. Thus, it is not necessarily appropriate to ascribe these anomalies only to the Kondo effect since the effect of the Kondo screening is considered to be small in such low-carrier materials. In this paper, we report on evidence of a type of heavy-electron property that is realized in the low-carrier system Yb_4As_3.

Yb_4As_3 has the anti-Th_3P_4-type cubic crystal structure (space group $I\bar{4}3d$) above about 290 K with the lattice constant a=8.78 Å. Below this temperature, it shrinks slightly along one of the ⟨111⟩ directions, giving a trigonal structure with α=90.8° (space group $R3c$).[3] In the trigonal phase, the electronic state of Yb_4As_3 is quite unusual.[4] The susceptibility of the compound shows the Curie-Weiss behavior at high temperatures, however, a tendency of saturation is seen below about 20 K. Then it increases again steeply, below about 7 K. However, the compound exhibits no long-range magnetic ordering down to 0.045 K.[5] It shows also a large T-linear term in specific heat (γ=205 mJ/K^2/mole) and a strong T-square dependence (A=0.75 $\mu\Omega$ cm/K^2) followed by a $-\ln T$ dependence in the electrical resistivity in the trigonal phase. The γ value vs susceptibility at about 10 K, where it shows a shoulder, as well as the A value vs γ^2 at low temperatures lie on the same lines as those of typical heavy-electron materials. These facts indicate that Yb_4As_3 can be well categorized as a heavy-electron material. The interesting point is that the carrier density in this compound is extremely low ($\sim 10^{-3}$ per formula) at low temperatures as described above.

On the other hand, the susceptibility,[4] Mössbauer,[5] and perturbed angular correlation[6] measurements suggest that the structural phase transition is accompanied by charge ordering from a valence fluctuating state in the cubic phase to a charge ordered state in the trigonal phase. Figure 1 illustrates the expected charge ordering in Yb_4As_3. In the cubic phase the crystal structure can be considered a dense cubic packing of equivalent cylinders,[7] in which four equivalent rods composed of linear chains of Yb ions on-site ($16c$) along ⟨111⟩ directions are packed very densely. With the trigonal distortion, the distance between Yb atoms becomes shorter in the chain along one of ⟨111⟩ axes and longer in the other three chains. It has been suggested that the charge order in Yb_4As_3 is such that Yb ions in the short chain (Yb_I) become trivalent, whereas those in the long chains (Yb_{II}) become divalent. The Yb_I and Yb_{II} atoms are shown by gray and white circles, respectively, in Fig. 1. They are crystallographically equivalent in the cubic phase. Our recent polarized neutron work revealed that, under a magnetic field of 5 T, the induced moment of Yb_I is seven to eight times bigger than that of Yb_{II} in the trigonal phase (for example, $0.19\mu_B$ and

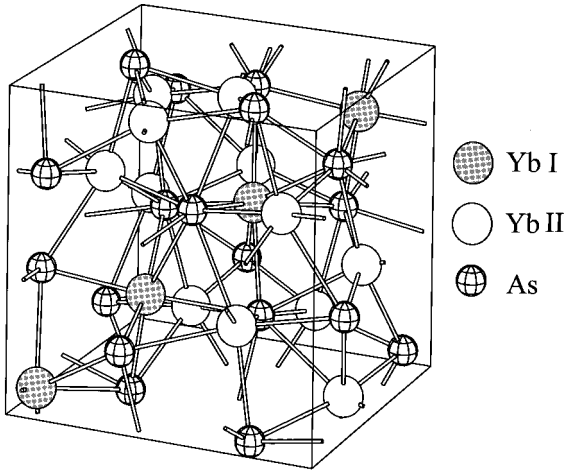

FIG. 1. Crystal structure of Yb_4As_3, illustrating the expected charge ordering in the trigonal phase ($T \leqslant 290$ K). In the cubic phase, Yb_I and Yb_{II} are equivalent. See text.

$0.03\mu_B$ at 1.3 K for Yb_I and Yb_{II}, respectively).[8] Since the electronic configuration of Yb^{2+} and Yb^{3+} ions are $4f^{14}$ and $4f^{13}$, respectively, Yb^{2+} is nonmagnetic, and the induced moment is a measure of the trivalency of the Yb ions. The result of the polarized neutron work clearly indicates that Yb_I is mainly trivalent whereas Yb_{II} is mainly divalent. Note that Yb_{II} still shows some amount of trivalency. In this sense, the charge ordering in Yb_4As_3 is imperfect even at low temperatures. The polarized neutron experiment also revealed that the increase of the susceptibility below about 7 K is not due to any impurity effect but is a bulk property. We have performed inelastic neutron-scattering experiments on this material in order to shed light on the electronic state of this material at low temperatures from the microscopic point of view. The results of the experiments are briefly described below.

First, we discuss the magnetic excitations in a wide energy range measured with a polycrystalline sample in order to know the crystal-field state of this material. The experiment was performed on the time-of-flight spectrometer LAM-D, installed at the pulsed neutron facility KENS, Tsukuba, with a large crystal analyzer mirror, the final energy of which is fixed at 4.6 meV. The observed spectra of Yb_4As_3 at 3.3 and 50 K with the scattering angle of $35° \pm 9°$ are shown in Fig. 2. In the spectrum at 3.3 K, four inelastic peaks are seen at about 3, 14, 21, and 29 meV. They show a decrease of peak intensity as well as a broadening of peak to the lower-energy side at 50 K. Since, in general, the ground multiplet of a Yb^{3+} ion, $^2F_{7/2}$, splits into four doublets under a crystal field in the present symmetry, the observed spectra as well as its temperature dependence can be explained by the energy scheme illustrated in the bottom of Fig. 2. Here, the upper three peaks at 14, 21, and 29 meV observed at 3.3 K are assigned to the crystal-field excitations from the ground state, and the low-energy peak around 3 meV corresponds to some magnetic excitation within the crystal-field ground doublet. The broadening of the upper peaks at 50 K is considered to be due to an increase of the probability of the excitations from the thermally populated initial states within the crystal-field ground doublet. It is noticed that the existence of the splitting of the ground doublet is unusual

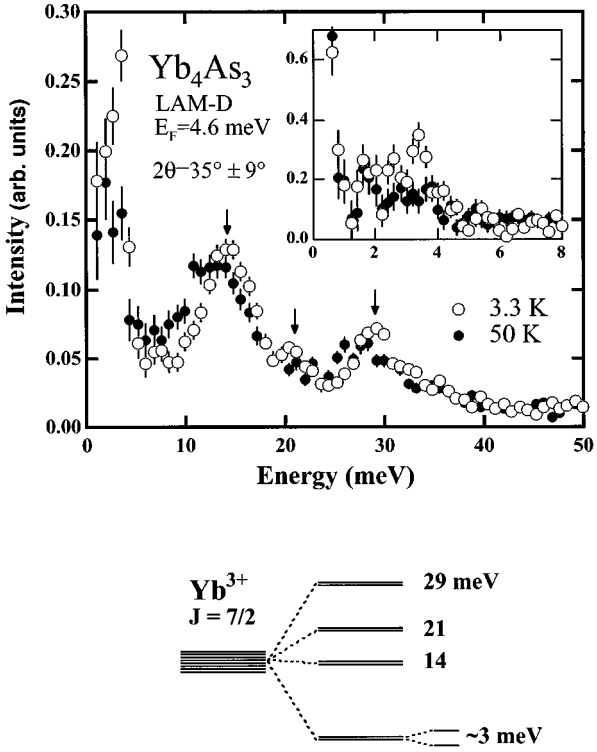

FIG. 2. Spectra of polycrystalline Yb_4As_3 measured at 3.3 K (open circles) and 50 K (closed circles). The low-energy part of the spectra is enlarged in the inset. Peaks indicated by arrows correspond to the crystal-field excitations (see the level scheme shown underneath the spectra panel).

since the system shows no magnetic long-range order. Actually, the low-energy peak has some structure, as seen in the inset of Fig. 2, and it develops remarkably below 20 K where a deviation of the susceptibility from the Curie-Weiss law is seen.

In order to clarify the origin of the unusual splitting of the crystal-field ground doublet, the low-energy magnetic response from Yb_4As_3 below about 7 meV was carefully investigated by using single-crystal samples of about 0.2 cm^3. The neutron-scattering experiments were performed at the triple-axis spectrometers 6G and C1-1 at the JRR-3M reactor in JAERI, Tokai, and 4F1 at the Orfée reactor in LLB, Saclay. The scattering was measured in the (hll) reciprocal lattice plane. In order to avoid the ambiguity due to domain distribution in the trigonal phase, where in general four domains are possible corresponding to four equivalent $\langle 111 \rangle$ directions in the cubic phase, the crystal was cooled through the structural phase transition point under a uniaxial stress along the [111] direction applied by sandwiching the crystal between two aluminum plates using small bolts and nuts with spring washers. The rocking curves of 800 and 022 Bragg peaks indicated the presence of an almost perfect single-domain sample in the trigonal phase.

Well-defined and strongly dispersive inelastic peaks were observed at various points in the scattering plane below about 20 K. It was found that the observed magnetic peaks can be well organized if the wave vectors of the excitations are taken as those defined for a one-dimensional Yb_I chain aligned along the [111] axis instead of taking the three-dimensional ones. In this case, the wave vector q is mea-

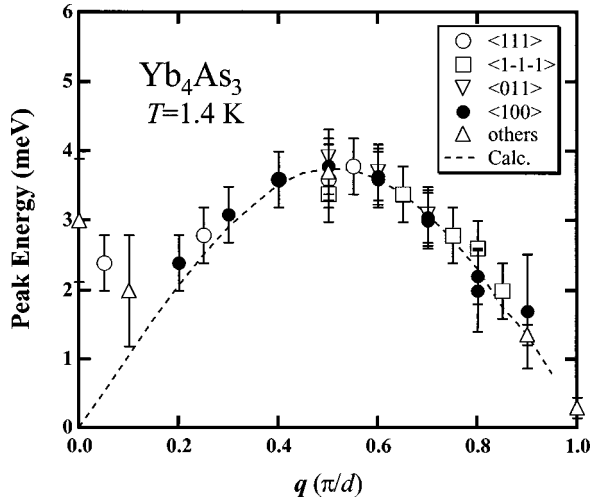

FIG. 3. Dispersion relation of inelastic peaks of Yb_4As_3 in the one-dimensional representation. Different symbols indicate different directions from the (200) reciprocal lattice point (see legend). The broken line represents the peak position calculated by the 1DHAF model.

sured along the [111] direction from the planes which are perpendicular to the [111] axis and are equally spaced by $2\pi/d$, where d (=3.8 Å) is the atomic distance in the Yb_I ion chain and one of the planes passes through the origin of the reciprocal space (scattering plane). In Fig. 3 the peak positions of the observed spectra at 1.4 K measured with the incident neutron energy of 13.7 meV are plotted against the wave vector q in the unit of π/d. Here, $q=0$ and 1 corresponds to the ferromagnetic and antiferromagnetic correlations of the magnetic moments of Yb_I ions, respectively. Although the data are taken at various positions in the three-dimensional reciprocal lattice space, their peak positions lie on a single curve. The result clearly indicates that the Yb^{3+} chains aligned along the [111] direction caused by the charge ordering behave as one-dimensional spin systems, and that the interaction between the Yb^{3+} chains is negligible.

The observed dispersion curve is quite close to a sine function except near the one-dimensional zone center ($q=0$). This fact suggests that the system may be modeled by a one-dimensional spin-1/2 Heisenberg system with a nearest-neighbor antiferromagnetic interaction (1DHAF). Thus, the observed spectra were compared with the dynamical spin-correlation function calculated by using the Müller ansatz for 1DHAF.[9] Here, the density of the spin excitations has a sharp lower bound at the energy of the so-called des Cloizeaux–Pearson spin-wave branch,[10] $E_1(q)=\pi J \sin(dq)$, and, above that energy, there is a continuum of excitations up to the energy of $E_2(q)=2\pi J \sin(dq/2)$. Figure 4 shows the observed spectra at various q values measured with the incident neutron energy of 13.7 meV. The dotted lines in Fig. 4 show the calculated spectra convoluted with the resolution function. Here πJ was taken to be 3.5 meV, and the calculated intensities are normalized to the data at $q=0.8$ shown in Fig. 4(g). The peak position of the calculated spectra is shown by the dotted curve in Fig. 3. The agreement between the observation and calculation is quite good not only for the dispersion relation but also for the spectral shape, except near $q=0$. It is especially noticed that

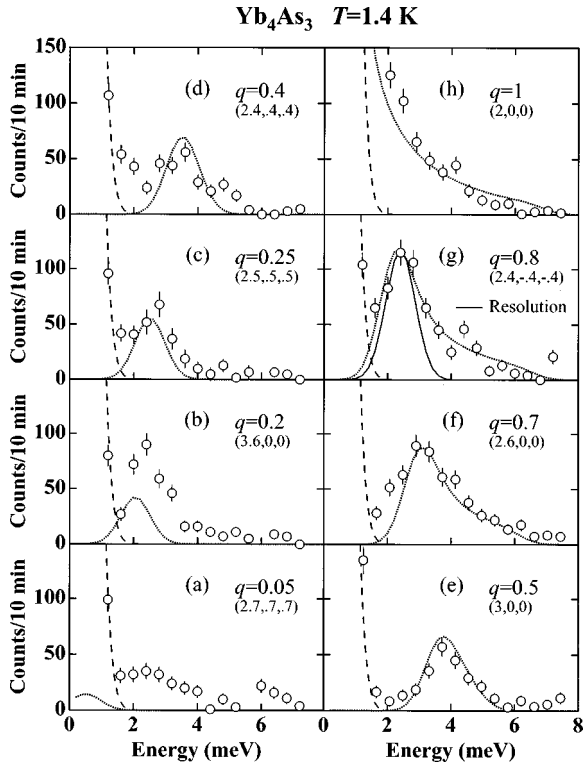

FIG. 4. Low-energy neutron spectra observed for Yb_4As_3 at 1.4 K. The measured point in the reciprocal lattice space for each scan is shown underneath the q value. The dotted lines denote the calculated intensity based on the 1DHAF model. The broken lines show the incoherent elastic peaks. The solid line in panel (g) indicates the resolution of the spectrometer.

the asymmetric spectra observed for the wave vectors near $q=1$ [see for example Figs. 4(f)–4(h)] are well explained by the existence of the continuum of the spin excitations characteristic of the 1DHAF model. The fact clearly indicates that the charge ordering causes a quite similar state to the 1DHAF system in Yb_4As_3. The response around $q=0$ [see for example Figs. 4(a) or 4(b)], which is not compatible with the 1DHAF model, may be due to some other origin since the excitation energy as well as the spectral density vanish at $q=0$ in the Heisenberg system. This point will be discussed later.

To our knowledge, this is the first observation that such a typical one dimensionality is realized in a three-dimensional rare-earth compound. Moreover, it is rather amazing that the observed spin excitations look so similar to those of the 1DHAF system in spite of the fact that the system is composed of $4f$ magnetic moments which show usually strong anisotropy due to crystal-field splitting. Concerning this point, it is also noticed that the 1DHAF model with $\pi J=3.5$ meV gives the C/T value of 0.19 J/K^2/mol at the low-temperature limit and a temperature of susceptibility maximum of 17 K.[11] These values are quite close to the observed γ value and the temperature at which the suppression of susceptibility is seen (disregarding the upturn below about 7 K), respectively. Thus, it is quite likely that the heavy-electron anomalies seen in these physical quantities are actually due to the 1DHAF properties of the Yb^{3+} chains caused by the charge ordering. The above experimental facts indicate that the system is quite close to an insulating one-dimensional antiferromagnet and that the unusual properties of this mate-

rial are strongly related to this situation. Fulde *et al.*[12] proposed that the charge ordering in Yb_4As_3 is due to the band Jahn-Teller effect. They derived a heavy mass of the lower band by treating the system with a t-J model taking into account the effect of the self doping of the Yb^{3+} chains due to interchain (Yb_I-Yb_{II} chains) interaction. The value of the mass is consistent with the observed heavy-electron properties of Yb_4As_3. Our experimental result is consistent with their theory at least in the sense that the 1DHAF properties found in our experiments are compatible with the spinon picture in the theory.

So far we have mainly discussed the experimental results from the side of the finding of the existence of the 1DHAF properties in the system. However, it is also clear that the system is not regarded as a simple 1DHAF one. The heavy-electron behavior of the electrical resistivity or the rather steep upturn of susceptibility below about 7 K (Ref. 4) are clearly out of the scheme of the 1DHAF model. The suppression of long-range magnetic ordering[5] is also unusual because, although the 1DHAF system does not show any long-range ordering, actual quasi-one-dimensional systems exhibit a three-dimensional magnetic long-range ordering at some temperature due to interchain interactions. These facts may be reflected in our neutron-scattering results. In fact, the existence of the unusual magnetic response around $q=0$ superimposed on the one-dimensional response seems to be consistent with the upturn of the susceptibility at low temperatures since the observed magnetic response at $q=0$ should contribute to additional susceptibility at low temperatures on that of the 1DHAF system which saturates at a finite value. The imperfection of the charge ordering observed by the polarized neutron experiment[8] may be also strongly related to the unusual properties.

It is now clear that all the unusual properties in Yb_4As_3 are due to the change of electronic state caused by the charge ordering in this particular crystal structure rather than due to the Kondo effect as thought in the early work on this material. The fact that the system exhibits the typical 1DHAF properties at low temperatures indicates that the electronic state in Yb_4As_3 becomes quite close to one of an insulating one-dimensional antiferromagnet by the charge ordering. On the other hand, the system is actually metallic, though the carrier density is extremely small, and the charge ordering in this system is not necessarily perfect. These facts strongly support the idea that the heavy-electron behaviors in Yb_4As_3 are regarded as unique phenomena in a state caused by the charge ordering which contains doped one-dimensional $4f^1$ hole chains with strong on-site f-electron correlations. In order to completely understand these interesting phenomena, more detailed experimental and theoretical studies are necessary.

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[1] P. Fulde, Physica B **230-232**, 1 (1997), and references therein.
[2] T. Suzuki, Physica B **186-188**, 347 (1993); *Physical Properties of Actinide and Rare Earth Compounds*, JJAP Series 8 (Jpn. J. Appl. Phys., Tokyo, 1993), p. 267, and references therein.
[3] S. Ono, J. G. Despault, L. D. Calvert, and J. B. Taylor, J. Less-Common Met. **22**, 51 (1970).
[4] A. Ochiai, T. Suzuki, and T. Kasuya, J. Phys. Soc. Jpn. **59**, 4129 (1990).
[5] P. Bonville, A. Ochiai, T. Suzuki, and E. Vencent, J. Phys. I **4**, 595 (1994).
[6] M. Rams, K. Królas, K. Tomala, A. Ochiai, and T. Suzuki, Hyperfine Interact. **97-98**, 125 (1996).
[7] M. O'Keeffe and S. Andersson, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **A33**, 914 (1977).
[8] M. Kohgi, K. Iwasa, A. Ochiai, T. Suzuki, J.-M. Mignot, B. Gillon, A. Gukasov, J. Schweizer, K. Kakurai, M. Nishi, A. Dönni, and T. Osakabe, Physica B **230-232**, 638 (1997).
[9] G. Müller, H. Thomas, and J. C. Bonner, Phys. Rev. B **24**, 1429 (1981).
[10] J. des Cloizeaux and J. J. Pearson, Phys. Rev. **128**, 2131 (1962).
[11] J. C. Bonner and M. E. Fisher, Phys. Rev. A **135**, 640 (1964).
[12] P. Fulde, B. Schmidt, and P. Thalmeier, Europhys. Lett. **31**, 323 (1995).