Incommensurate Magnetic Phase in $EuAs_3$ with Zone-Boundary Lock-in

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A new incommensurate magnetic phase has been found in europium triarsenide which belongs to a novel class of layered semimetallic compounds. This incommensurate phase develops below $T_N = 11.30$ K and is followed by a lock-in transition to a commensurate phase at $T_L = 10.26$ K. Although this happens at a zone-boundary wave vector, the transition is nearly continuous. We propose an interpretation of the very smooth temperature dependence of the modulation vector in terms of the soliton lattice model.

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In many $4f$ and $5f$ systems with local moments, competing exchange interactions lead to modulated magnetic structures with a temperature-dependent modulation vector $\mathbf{q}_m$. Empirically one can distinguish "staircase" behavior where $\mathbf{q}_m(T)$ takes only commensurate (C) values, as in the Ce pnictides,[1] from genuine incommensurate (IC) behavior where $\mathbf{q}_m(T)$ varies smoothly as in the heavy rare-earth (RE) metals. [2] In the latter case a Landau description is appropriate and if the moments are pinned along a crystal axis, e.g., the y axis, by an anisotropy, one is led to the "soliton lattice" (SL) picture[3,4] described by an order parameter

$$S(\mathbf{r}) = Ae^{i\phi(z)}e^{i\mathbf{q}_0\mathbf{r}}, \quad (1)$$

where $A^2 \sim T_N - T$, and $\phi(z)$ describes modulation of moments parallel to the y axis along the z direction; $\mathbf{q}_0$ is the C–lock-in wave vector. Immediately below the Néel temperature T_N, $\phi(z) = \delta \cdot \mathbf{r}$ where $\delta = \mathbf{q}_m - \mathbf{q}_0$ is parallel to $\hat{\mathbf{z}}$. At temperatures slightly above the lock-in temperature T_L, $\phi(z)$ is almost constant in a large range of z (C regions) separated by narrow regions (called phase solitons or domain walls) where $\phi(z)$ increases rapidly to reach the next C value $n(\pi/2)$. The corresponding $\delta(T)$ is determined by the density of solitons as described by the sine-Gordon equation and it is a smooth function of temperature.

In this Letter, we report on the observation of a new IC magnetic phase in $EuAs_3$ in which the modulation vector varies smoothly with temperature in a range $T_L < T < T_N$ and becomes locked at the zone boundary at T_L. We examine the experimental results in the light of the SL model introduced above.

Semimetallic $EuAs_3$ and the mixed crystals $Eu_xSr_{1-x}As_3$ and $Eu(As_xP_{1-x})_3$ are a new class of layered compounds with very exciting magnetic properties that makes them as interesting as the Ce pnictides. Besides the zero-field IC phase reported in this paper, $EuAs_3$ shows a great variety of C and IC regions in the H-T phase diagram which are not yet understood. The Sr-diluted crystals have an anisotropic spin-glass phase with a very anomalous specific-heat behavior.[5] It seems likely that the anisotropy of exchange interactions plays an important role in these compounds. This may also be connected to the anisotropic electronic properties of $EuAs_3$.[6]

The structure of $EuAs_3$ is monoclinic (Fig. 1) and may be described as chains of Eu atoms running through tubes formed by folded layers of As atoms. The Eu sublattice, however, has a three-dimensional character. The Eu^{2+} ions are in an $^8S_{7/2}$ ground state with no orbital contribution to the magnetic moment of $7\mu_B$. Specific-heat measurements have shown that $EuAs_3$ has two successive phase transitions at $T_N = 11.30$ K and at $T_L = 10.26$ K. The phase stable below T_L is found by neutron diffraction to be antiferromagnetic (AF1).[7] It is shown in Fig. 1 in which full and open circles represent Eu atoms with moments pointing along the monoclinic $\pm\mathbf{b}$ directions. It can be obtained by modulation of the unit-cell spin config-

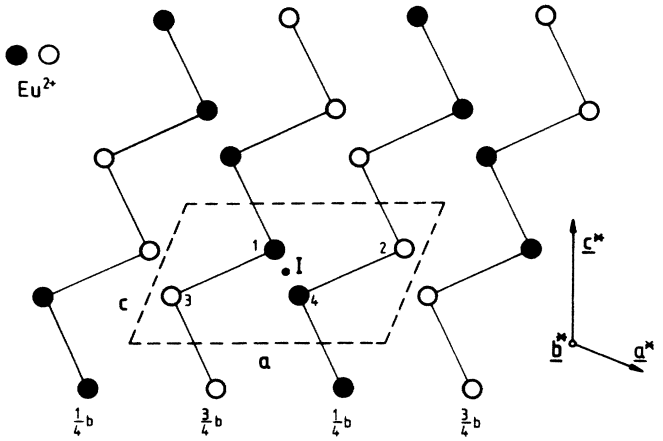

FIG. 1. Crystal structure and magnetic low-temperature phase of $EuAs_3$. (As atoms are not shown.) Chemical unit cell (atoms 1–4, basis vectors **a**, **b**, **c**) is indicated by dotted lines; **b** is perpendicular to the plane. The reciprocal lattice is denoted by **a***, **b***, **c***. Crossed circle corresponds to the inversion center. Magnetic moments are parallel (open circles) and antiparallel (full circles) to **b**. $(\bar{2}01)$ planes are ordered ferromagnetically.

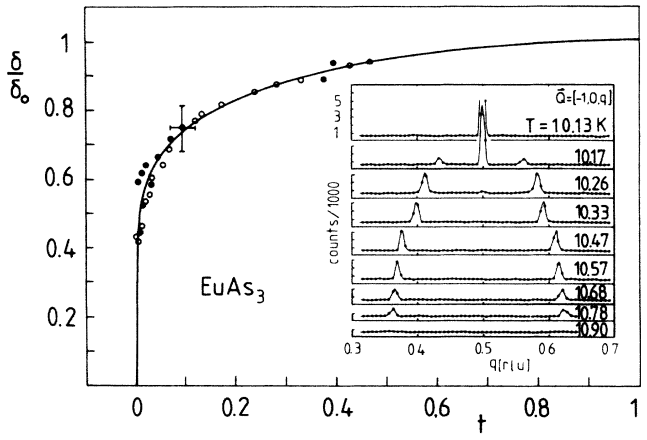

FIG. 2. Temperature dependence of satellite reflexes $[\bar{1},0,\frac{1}{2}\pm\delta]$. Open and closed circles correspond to cooling and heating cycles, respectively. Full line, sine-Gordon SL theory. Extrapolated scale value: $\delta_0=0.15$, $t=(T-T_L)/(T_N-T_L)$ (reduced temperature). Experimental error bars are indicated. Inset: Temperature variation of scattering intensity for a **q** scan parallel to **c*** around the low-temperature AF Bragg reflection $[\bar{1}0\frac{1}{2}]$.

uration sinusoidally with a C wave vector $\mathbf{q}_0=\frac{1}{2}\mathbf{c}^*$.

To characterize the intermediate phase, stable in the range $T_L<T<T_N$, we have made additional neutron diffraction measurements using the D15 diffractometer at the high-flux reactor of the Institut Laue Langevin in Grenoble. A single crystal of size $1\times1\times5$ mm^3 elongated parallel to **b** was used. The diffractometer was used in normal beam geometry at a wavelength $\lambda=1.174$ Å with the crystal needle axis parallel to the ω axis of the diffractometer to reduce the effect of the strong absorption of $EuAs_3$ crystals ($\mu=35$ cm^{-1}) synthesized with natural Eu atoms. However, the intensities of the reflections were corrected for absorption effects. Refinement of the nuclear structure led to an agreement factor $R=5\%$ between the observed and calculated structure factors indicating the absence of strong extinction effects. The C-AF1 phase which has moments parallel to **b** gives a strong magnetic Bragg reflection at the reciprocal point $[\bar{1}0\frac{1}{2}]$ indexed with respect to the chemical cell. The intensity of this reflection decreases with increasing temperature according to the square of the Brillouin function $B_{S=7/2}$ until $T_L=10.26$ K, where it drops to zero abruptly suggesting a first-order transition. In the inset of Fig. 2 the intensities obtained in q scans parallel to **c*** through $[\bar{1}0\frac{1}{2}]$ are shown as a function of temperature. At 10.13 K only the peak of the commensurate AF1 phase is observed. At 10.17 K a pair of satellites at $[\bar{1},0,\frac{1}{2}\pm\delta]$ starts to develop which increases very rapidly in intensity and moves away from the Bragg peak $[\bar{1}0\frac{1}{2}]$ as temperature rises above T_L. The satellite intensity decreases again at higher temperature and can no longer be observed above 10.9 K. The separation of satellites increases continuously with temperature until they disappear. The wave vector $\mathbf{q}_m=q_m\mathbf{c}^*$ where $q_m=\frac{1}{2}-\delta$ varies continuously from $q_m=0.35$ at T_N to the commensurate value $q_m=\frac{1}{2}$ at T_L. The value of q_m was determined in both heating and cooling cycles and no significant hysteresis was observed. The temperature stability in these measurements was about ±0.02 K and the wave vector was determined with an accuracy of about ±0.01 reciprocal lattice units.

The results show that the intermediate magnetic phase of $EuAs_3$ is an IC antiferromagnetic phase with a wave vector $q_m\mathbf{c}^*$ which undergoes a continuous lock-in transition (except for an apparent jump at T_L discussed later) to a C-AF1 phase characterized by a zone boundary vector with $q_m=q_0=\frac{1}{2}$. More detailed measurements showed the actual position of IC reflections at $[\overline{1.05},0,q_m]$ and $[\overline{0.95},0,1-q_m]$, with $q_m=\frac{1}{2}-\delta$ corresponding to a two-legged star of the modulation wave vector $\pm(-0.05,0,q_m)$ with a temperature-independent x component instead of $\pm(0,0,q_m)=\pm q_m\mathbf{c}^*$. This means that the modulation direction is slightly tilted against the crystallographic **c*** direction. For simplicity we will neglect this additional component in the discussion. No second- or higher-order satellites were observed. If a second-order satellite exists it has less than 5% of the intensity of the first-order satellite at 10.4 K. The intensities of 95 independent primary satellites were measured and were found to follow quite closely the intensities of the

parent reflections in the AF1 phase. A model was therefore chosen in which the relative orientations of europium moments within one chemical unit cell are the same as in the AF1 phase but are sinusoidally modulated from cell to cell with wave vector $\mathbf{q}_m$. Two types of modulations were tried: (i) Directions of moments lying in (010) planes are sinusoidally modulated (spiral model); (ii) moments are held parallel to [010] and are modulated sinusoidally (linear model). The linear model gave significantly better agreement than the spiral model and also than any other model which was tried. Using the linear model we have refined the moment of the Eu atoms obtaining an agreement factor $R = 11\%$ between observed and calculated structure factors and an amplitude of $3.3\mu_B$ for the modulated moment distribution at $T = 10.35$ K. This corresponds to the rms moment of $2.3\mu_B$ per Eu atom. The extrapolated value of the Eu^{2+} moment according to the Brillouin curve at 10.35 K is $2.7\mu_B$. In the incommensurate phase we have therefore about 15% less ordered moment than would be expected if the magnetic structure stayed commensurate.

We have performed model calculations to understand the origin of the modulated structure. Because Eu^{2+} is an S-state ion we assume a Heisenberg exchange Hamiltonian

$$H_{ex} = -\tfrac{1}{2} \sum_{ll'\alpha\alpha'} I_{ll'}^{\alpha\alpha'} \mathbf{S}_l^{\alpha} \cdot \mathbf{S}_{l'}^{\alpha'} \quad . \tag{2}$$

Here l,l' refer to the unit cell and $\alpha,\alpha' = 1,\ldots,4$ to the basis atoms. In addition there is a single-ion anisotropy which leads to an easy axis parallel to $\mathbf{b}$ in the ordered state; it will not be included explicitly. The exchange tensor in Eq. (2) is parametrized by three phenomenological constants which are chosen in a way to satisfy obvious constraints given by the low-temperature AF1 phase. This phase consists of $(\bar{2}01)$ ferromagnetic planes stacked antiferromagnetically along the $[\bar{2}01]$ direction. For the in-plane nearest-neighbor (nn) coupling, $I_1 > 0$ is assumed and $I_2 < 0$ for the next-nearest-neighbor coupling to adjacent planes (Fig. 1). There is a single out-of-plane nn coupling I_0 left which should have the same sign ($I_0 > 0$) as the in-plane nn coupling but may have different magnitude. The out-of-plane nn coupling is frustrated in the low-temperature AF1 phase. Immediately below T_N this frustration could lead to an energetically more favorable incommensurate phase. It is convenient to use the "competition ratio" $r = -I_2/I_1$ and "anisotropy ratio" $r' = I_0/I_1$. A phase diagram of possible magnetic phases in the exchange-parameter plane is obtained for $T \lesssim T_N$ by calculation of the $\mathbf{q}$-dependent mean-field susceptibility. Details of this model will be given elsewhere.[8] The phase diagram is shown in Fig. 3. An IC phase is found to be possible in a sector of the (r,r') plane with $r > 1$ and $r' > 4$. The IC wave vector $\mathbf{q}_m = q_m\mathbf{c}^*$ and T_N are given by

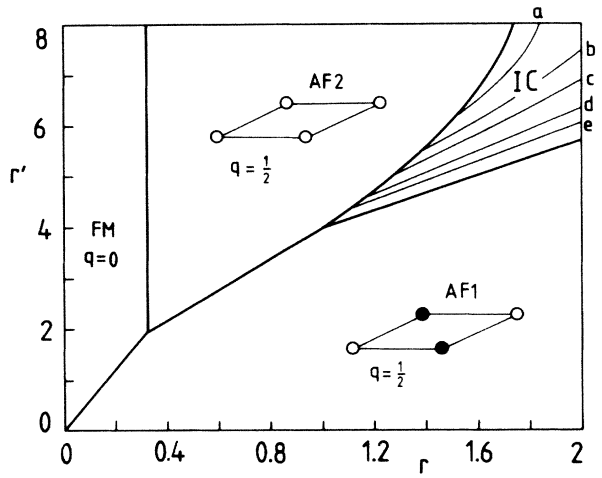

FIG. 3. Phase diagram for $T \lesssim T_N$ in the (r,r') parameter plane. AF1, AF2 are different antiferromagnetic C phases. FM, ferromagnetic phase. IC region is shown with contours for $\delta(r,r') = \frac{1}{2} - q_m$ [cf. Eq. (3)]. Curves a–e: $\delta = 0.14$, 0.13, 0.12, 0.11, 0.10, respectively.

$$q_m = \tfrac{1}{2}\cos^{-1}\left\{\frac{(1+r)(r'-r-2)}{8r^2} - \frac{1+r}{2(r'-r-2)} - \frac{r'-r-2}{2(1+r)}\right\},$$

$$k_B T_N = CI_1\left\{2r + \frac{(1+r)(r'-r-2)}{4r} + \frac{r(1+r)}{r'-r-2} + \frac{r(r'-r-2)}{1+r}\right\}, \tag{3}$$

with $C = \frac{1}{3}S(S+1)$. Numerically $\delta = \frac{1}{2} - q_m \lesssim 0.145$ in the IC sector which is close to the extrapolated experimental value $\delta_0 = \delta(T_N) = 0.15$. Below the IC sector the calculated first magnetic phase is a C phase with $\mathbf{q}_0 = \frac{1}{2}\mathbf{c}^*$ ($q_0 = \frac{1}{2}$) and is identical with the observed AF1 phase for $T < T_L$. Above the IC region one obtains a different antiferromagnetic structure AF2 not observed. In addition, a small ferromagnetic region FM exists. For isotropic nn exchange ($r' = 1$) only an FM or AF1 phase but no IC phase exists. The ratios r,r' cannot yet be determined unambiguously. Comparison with susceptibility data[6,8] suggests that (r,r') lies in the lower part of the IC sector. Choosing $(r,r') = (1.6, 5.7)$ one obtains $\delta_0 = 0.12$. With I_1 determined from T_N we have

$$I_0 = 1.66 \text{ K}, \quad I_1 = 0.29 \text{ K}, \quad I_2 = -0.47 \text{ K}.$$

The out-of-plane coupling I_0 is rather large. It should be considered as an effective coupling which also includes the influence of a ferromagnetic coupling to the next higher $(\bar{2}01)$ planes (see Fig. 1), so that the real I_0 would be smaller than given above. This raises the important question about the microscopic origin of exchange anisotropy of the Eu^{2+} S-state ions in semimetallic $EuAs_3$. Apart from conventional effective exchange mechanisms, f-p hybridization resulting from the proximity of f states to the Fermi level might be important—similar to the case in CeSb.[9]

The smooth variation of $\delta(T)$, the existence of only one lock-in C phase, and the observation that T_L is only ~ 1 K below T_N, i.e., $(T_N - T_L)/T_L \ll 1$, suggest that $EuAs_3$ is an excellent example of a Landau description where the free energy can be expanded in terms of the order parameter of Eq. (1). Because the lock-in transition happens at a zone-boundary vector $\mathbf{q}_0 = \frac{1}{2}\mathbf{c}^*$, one would naively expect a free-energy functional as described by Bruce, Cowley, and Murray[10] which leads to a sudden steplike lock-in at T_L without any T dependence of δ, in clear contradiction to the experimental situation. A detailed investigation shows, however, that one obtains a "sine-Gordon" functional $F_{SG}[\phi]$ for the free energy because there are two independent complex order-parameter components corresponding to two inequivalent sites along $\mathbf{c}$ in the unit cell of Fig. 1. This functional has been thoroughly investigated[3,4] and it leads to a smooth $\delta(t)$ behavior with $\delta(t) \sim |\ln t|^{-1}$ for $t \to 0$ where $t = (T - T_L)/T_N - T_L)$ is the reduced temperature. In Fig. 2 we show the calculated $\delta(t)$, which is a universal function independent of Landau parameters,[3] compared to the experimental values for $EuAs_3$. The agreement is excellent over the whole temperature range. There is no fit parameter in the theory except for a scale parameter $\delta_0 = \delta(T_N)$ which was extrapolated such that the first datum point below T_N lies on the theoretical curve. Although the SL picture explains $\delta(t)$ very well there are some problems with this interpretation:

(i) It seems that the lock-in transition at T_L is not really continuous but is ultimately of first order. However, the $\delta(t)$ function of the SL model which is in principle continuous for $t \to 0$ $(T \to T_L)$ is virtually indistinguishable from a discontinuous first-order lock-in transition because of the logarithmic behavior of $\delta(t)$. For example, when $\delta(t)/\delta_0 \simeq 0.4$ (last experimental points in Fig. 2) one has $t \simeq 10^{-3}$ for the theoretical curve,[3] i.e., T is extremely close to the continuous lock-in temperature. Furthermore, interaction of spins with the lattice might indeed lead to a lock-in transition which is of first order.[11]

(ii) If the temperature decreases appreciably below T_N, secondary satellites due to higher harmonics of the distorted phase $\phi(z)$ in the SL model should in principle occur. As mentioned above they have not been identified; possibly their intensity is too low unless one is close to T_L. In fact just before lock-in a splitting of the primary IC satellite into a double-peak structure was observed. This point needs further experimental investigation. Despite these reservations the soliton lattice model seems to be the most attractive one to explain the T-dependent modulation vector in the IC phase.

In conclusion, $EuAs_3$ is a new incommensurate antiferromagnet which belongs to a class of magnetic layered compounds that promise to be as exciting as the Ce pnictides. Although the C lock-in transition happens at the zone boundary, the modulation vector shows a nearly continuous T dependence which is adequately described by the SL model. Further investigation about the role of anisotropy of the exchange coupling and its origin, possibly by inelastic neutron scattering experiments, is necessary.

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[1]J. Rossat-Mignod, P. Burlet, J. Quezel, J. M. Effantin, D. Delacôte, H. Bartholin, O. Vogt, and D. Ravot, J. Magn. Magn. Mater. **31–34**, 398 (1983).

[2]B. Coqblin, *The Electronic Structure of Rare Earth Metals and Alloys: the Magnetic Heavy Rare-Earths* (Academic, London, 1977).

[3]W. L. McMillan, Phys. Rev. B **14**, 1496 (1986).

[4]P. Bak and J. v. Boehm, Phys. Rev. B **21**, 5297 (1980).

[5]A. Schröder, H. v. Löhneysen, and W. Bauhofer, to be published.

[6]W. Bauhofer, E. Gmelin, M. Möllendorf, R. Nesper, and H. G. v. Schnering, J. Phys. C **18**, 3017 (1985).

[7]T. Chattopadhyay, H. G. v. Schnering, and P. J. Brown, J. Magn. Magn. Mater. **28**, 247 (1982).

[8]P. Thalmeier, J. Magn. Magn. Mater. **58**, 207 (1986).

[9]H. Takahashi and T. Kasuya, J. Phys. C **18**, 2697 (1985).

[10]A. D. Bruce, R. A. Cowley, and A. F. Murray, J. Phys. C **11**, 3591 (1978).

[11]M. Gordon and J. Villain, J. Phys. C **13**, 3117 (1980).