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Sine-wave–to–helimagnetic transition in phosphorus-rich $Eu(As_{1-x}P_x)_3$

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Neutron-diffraction experiments on phosphorus-rich $Eu(As_{1-x}P_x)_3$ have established that the ordered magnetic phase just below T_N (8.5 K) is a sine-wave phase which undergoes a first-order phase transition at about 7.5 K to a helimagnetic phase. This is the first observation of such a sine-wave–to–helical phase transition in real magnetic system.

Incommensurate magnetic structures can be described as the long period modulations of ferro- or antiferromagnetic structures which are commensurate with the crystal lattice. Incommensurate structures have been observed in many magnetic systems.[1,2] The irreducible representation corresponding to an incommensurate wave vector which becomes critical at the ordering temperature cannot have a dimension larger than two. The associated order parameter must be either one or two dimensional and therefore, two types of incommensurate structures appear: sine-wave and helical modulations corresponding to one- and two-dimensional order parameters, respectively. The commensurate structure is characterized by the wave vector **K** belonging to some symmetry point of the Brillouin zone whereas the incommensurate structure is characterized by the wave vector **K**+**k** where **k** is usually small. Under the influence of temperature or magnetic field, the incommensurate structure can undergo a lock-in transition to the commensurate structure with either a continuous or discontinuous variation of the incommensurate vector **k** which goes to zero at the transition temperature. This type of lock-in transition has been studied in many magnetic systems.[1-3] For orthorhombic or lower symmetry all the irreducible representations are one dimensional and hence, helimagnetic ordering cannot develop at T_N in a second-order transition; an incommensurate phase which develops at T_N must therefore be a sine-wave modulation. At lower temperatures a further transition to a helimagnetic structure may occur. Such a transition may take place very close to T_N when isotropic exchange interactions dominate the anisotropic ones. In this Rapid Communication we report the first observation of such a sine-wave–to–helical phase transition in a real magnetic system—$Eu(As_{1-x}P_x)_3$.

Semimetallic $EuAs_3$ and its solid solutions with EuP_3 form a very interesting magnetic system.[3-9] The magnetic phase diagram of $EuAs_3$ and $Eu(As_{1-x}P_x)_3$ is surprisingly complex for Eu^{2+} in the $^8S_{7/2}$ ground state. $EuAs_3$ orders with a second-order phase transition at $T_N=11.4$ K to an incommensurate sine-wave phase.[3] The wave vector of this sine-wave phase changes continuously with decreasing temperature and eventually locks into a commensurate phase at $T_L=10.3$ K. This lock-in transition exists also in $Eu(As_{1-x}P_x)_3$ at least up to $x=0.40$. However, for phosphorus-rich $Eu(As_{1-x}P_x)_3$ no lock-in transition takes place and instead a sine-wave–to–helimagnetic transition has been observed (Fig. 1). We have studied this transition in two samples with $x=0.80$ and 0.98.

$Eu(As_{1-x}P_x)_3$ has been synthesized from the elements using Eu of 99.9% purity, and As and P of 99.999% purity as starting materials. Large single crystals were grown by the Bridgman technique. Needle-shaped single crystals 1 mm×1 mm×5 mm with needle axis parallel to either the *b* or *a* axes were cut out of larger crystals. Neutron-

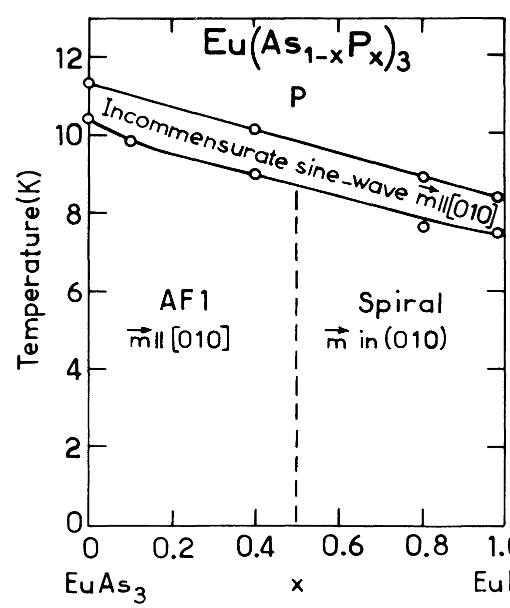

FIG. 1. Magnetic (T,x) phase diagram of the system $Eu(As_{1-x}P_x)_3$.

TABLE I. Magnetic structures of $Eu(As_{0.02}P_{0.98})_3$. α is the angle between the major axis of the ellipse and the a^* direction; S_x,S_y are the components of the magnetic moments along the major and minor axes of the ellipse; S_z is the component of the magnetic moment parallel to $\pm$[010]; N is the number of independent reflections; R is the agreement factor.

Compound	T (K)	Wave vector	Moment direction	α (deg)	S_x (μ_B)	S_y (μ_B)	S_z (μ_B)	N	R
$Eu(As_{0.2}P_{0.98})_3$	4.0	[−0.726,0,0.222]	In (010) plane	99(1)	7.3(2)	4.5(1)	0	209	0.15
· · ·	7.5	[−0.726,0,0.255]	± [010]		0	0	3.9(1)	46	0.11

diffraction measurements were carried out using the D15 diffractometer at the high-flux reactor of the Institut Laue-Langevin in Grenoble. The crystal needle axes were aligned parallel to the ω axis of the diffractometer to reduce the effect of strong absorption of natural Eu ($\mu \simeq 35$ cm^{-1}).

Specific-heat and ac susceptibility measurements[4] have already shown the presence of two transitions in $Eu(As_{0.02}P_{0.98})_3$ at about 7.4 and 8.5 K. Neutron-diffraction experiments on $Eu(As_{0.02}P_{0.98})_3$ at 4.0 K showed the presence of magnetic satellites at positions near those of the magnetic peaks corresponding to the commensurate AF1 phase of $EuAs_3$ which has wave vector $[-1,0,\frac{1}{2}]$. The wave vector at 4.2 K was determined from the positions of several strong magnetic reflections as [−0.726,0,0.222]. Intensities of 209 independent magnetic reflections from the two crystals with needle axes parallel to the b and a axes were measured at 4.0 K. Two structure models were tried: (a) spin-orientations, held in (010) plane, are sinusoidally modulated (helical or elliptic spiral model) and (b) the amplitude of the spins held parallel to ± [010] direction, are modulated sinusoidally (sine wave). In these models the relative orientations of the spins of Eu atoms in one chemical cell is the same as in the AF1 phase of $EuAs_3$ but are modulated from cell to cell. Model (a) gave a significantly better agreement factor $R=0.15$ compared to the $R=0.21$ for model (b). The components of the magnetic moments refined with the model (a) are $S_x=7.3(2)\mu_B$, $S_y=4.5(1)\mu_B$ and the angle α between the a^* axis and S_x is refined to be $\alpha=99(1)°$. The spins of the Eu atoms are modulated in amplitude and orientation having an elliptical envelope whose major axis makes an angle of 99° to the a^* axis or equivalently 9° to the c-axis in obtuse β (Table I).

The magnetic phase stable in the temperature range 7.4–8.5 K is also incommensurate with a wave vector [−0.726,0,0.255] which only differs slightly from that of the low-temperature phase. Intensities of 46 independent reflections were measured from two single crystals at 7.5 K. In this case, the sine-wave model with spin directions parallel to ± [010] described above gave the best agreement factor $R=0.11$ compared to $R=0.28$ obtained with spiral elliptic (helical) model. The amplitude of the modulated moment obtained using the sine-wave model is $3.9(1)\mu_B$ which corresponds to the rms value of $2.8\mu_B$.

The first magnetic phase of $Eu(As_{0.02}P_{0.98})_3$ below $T_N=8.5$ K is, therefore, a sine-wave phase with magnetic moments parallel to ± [010] direction. At about 7.4 K a phase transition to a helical phase takes place. The magnetic moments flip from the ± [010] direction to the (010) plane. Figure 2 shows the temperature variation of the intensity of the −0.726,0,0.222 reflection. The intensity of this reflection decreases continuously as the temperature is raised. At 7.5 K a discontinuity in intensity is observed. This corresponds well with the anomaly observed in the specific heat at about the same temperature. The magnetic-phase transition at $T=7.5$ K is, therefore, of first order. Between 7.5 K and $T_N=8.5$ K the intensity variation is found to be continuous and corresponds to a second-order phase transition at $T_N=8.5$ K. In the same figure temperature variation of the component l of the wave vector parallel to c^* is shown. This component of the wave vector increases continuously with temperature

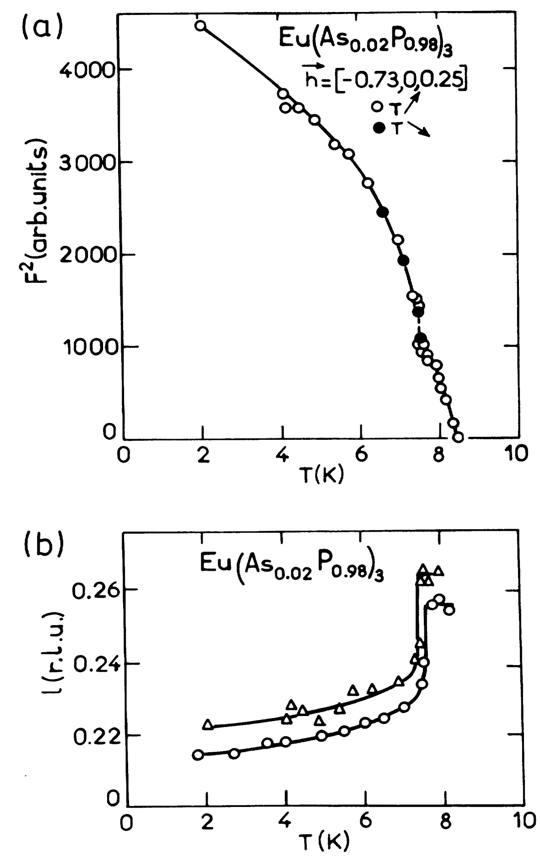

FIG. 2. Temperature dependence of (a) the intensity of the satellite −0.73,0,0.25 reflection and (b) the component of the wave vector parallel to c^* of $Eu(As_{0.02}P_{0.98})_3$ (two independent measurements are indicated by ○ and △). The discontinuities in these curves correspond to the first-order phase transition from the sine-wave phase to the helimagnetic phase at about 7.5 K.

from the low-temperature value of about 0.22 until at $T=7.5$ K it undergoes an abrupt increase from 0.24 to 0.26 corresponding to the first-order transition (helimagnetic to sine wave). The component of the wave vector parallel to a^* is found to be temperature independent within experimental error.

Neutron-diffraction experiments on $Eu(As_{0.20}P_{0.80})_3$ gave qualitatively similar results. At $T_N=8.9$ K a sine-wave phase develops which undergoes a transition to a helimagnetic phase (elliptic spiral) at about $T=7.65$ K. The wave vector of the sine-wave phase [0.815,0,0.301] is temperature independent in contrast to the wave vector of the sine-wave phases of $EuAs_3$ and arsenic-rich $Eu(As_{1-x}P_x)_3$. The wave vector of the helical phase at 1.48 K is found to be [−0.790,0,0.250]. Again, the component h of the wave vector parallel to a^* is temperature independent whereas the component 1 parallel to c^* increases as the temperature is raised. Figure 3 shows the temperature variation of the intensity of the satellite reflection and the component of the wave vector parallel to c^*. These temperature variations are qualitatively the same as those of $Eu(As_{0.02}P_{0.98})_3$ given in Fig. 2. However, the intensity and the wave-vector variation at the sine-wave to helimagnetic transition is more pronounced.

The observation of sine-wave–to–helimagnetic phase transitions in phosphorus-rich $Eu(As_{1-x}P_x)_3$ indicates a surprising complexity in the temperature-concentration phase diagram of this system, since at lower P concentrations ($x \leq 0.4$) it is known that the sine-wave phase undergoes a lock-in transition to a commensurate phase. At the present time the details of the phase diagram in the region between these two regions are not known, but if no further magnetic phases are present then there must be a line in the diagram on which the commensurate and helimagnetic phase co-exist and a triple point at which all three phases co-exist. That this is the case receives support from our recent observation of a pressure-induced phase transition in $EuAs_3$ at about 17 kbar (Ref. 8) from the commensurate phase to a helimagnetic phase almost identical to that found in the phosphorus-rich solid solution. Such parallelism between the behavior under pressure, and with varying phosphorus concentration, can be correlated with the smaller size of P relative to As atoms producing an equivalent "chemical pressure." However, the reason why the helimagnetic structure should be favored relative to the commensurate one under pressure is not understood at present.

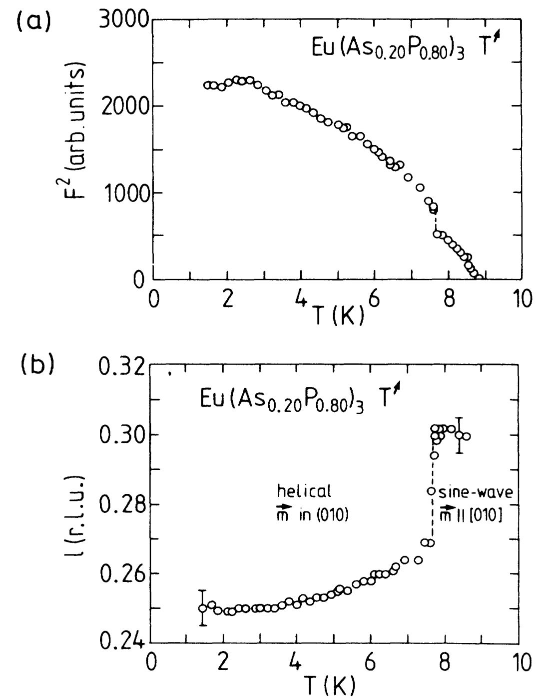

FIG. 3. Temperature dependence of (a) the intensity of the satellite −0.79,0,0.25 reflection and (b) the component of the wave vector parallel to c^* of $Eu(As_{0.20}P_{0.80})_3$. The discontinuities in these curves are much more prominent than those of $Eu(As_{0.02}P_{0.98})_3$ and correspond to the first-order phase transition from the sine-wave phase to the helimagnetic phase at about 7.6 K.

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