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1990 J. Phys.: Condens. Matter 2 10211

(http://iopscience.iop.org/0953-8984/2/50/026)

J. Phys.: Condens. Matter 2 (1990) 10211–10216. Printed in the UK

LETTER TO THE EDITOR

The magnetic structure of $CeAl_2$ is a non-chiral spiral*

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Received 9 October 1990

Abstract. The previously accepted spatially modulated magnetic structure of $CeAl_2$ is shown to be incorrect. Neutron diffraction measurements in an applied magnetic field imply that the zero-field magnetic structure is spiral: however, the moments on the two Ce sublattices rotate in opposite senses. In our model, the magnitude of the Ce ordered moment varies little from site to site; a non-magnetic ground state for the Ce^{3+} ion is no longer required, and the extreme weakness of the harmonics is explained.

The nature of the magnetism of $CeAl_2$ has excited great interest for many years: on the one hand, it appears to display many of the characteristics of an intermediate-valence compound, showing resistance anomalies [1] and a large linear term in the heat capacity [2]; on the other hand, it orders into an antiferromagnetic structure below 3.8 K. According to Barbara *et al* [3], this magnetic structure is sinusoidally modulated with wavevectors of the form $\{\frac{1}{2}+\delta, \frac{1}{2}-\delta, \frac{1}{2}\}$, where $\delta \sim 0.110$. One remarkable feature of the neutron diffraction is the extreme weakness of the higher harmonic satellites, even down to the lowest temperatures. This is quite unexpected on thermodynamic grounds, since the sinusoidal modulation should square up as $T \rightarrow 0$. The existence of a modulated ground state and the weakness of the harmonics have been taken as additional evidence for the near instability of the 4f moment [4]: in this view, the occurrence of sites with small or zero moments as $T \rightarrow 0$ is related to the formation of a non-magnetic Kondo singlet ground state.

By observing the effects of a magnetic field on the neutron diffraction pattern of $CeAl_2$ below 3.8 K, we have shown that the zero-field magnetic structure is not that proposed in [3]. The most natural interpretation of our results is a spiral structure with a much more constant magnitude of the Ce moment. This, then, does not require the controversal non-magnetic ground state for the Ce ion in this material.

Before giving an account of our experiments, it is necessary to describe in more detail what is already known from neutron diffraction about the magnetic structure of $CeAl_2$. The set of wavevectors described in [3] gives rise to hexagonal patterns of magnetic satellites around $\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$-type reciprocal lattice points. These satellites lie on FCC Brillouin zone faces as shown in figure 1. A good fit to the intensities of powder diffraction data

* Experimental work performed at the Institut Laue–Langevin, Grenoble, France.

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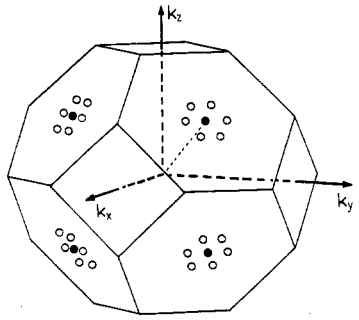

Figure 1. The FCC Brillouin zone of $CeAl_2$, showing the positions in reciprocal space of magnetic satellites (open circles) on the hexagonal faces of the zone. The filled circles are $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ points.

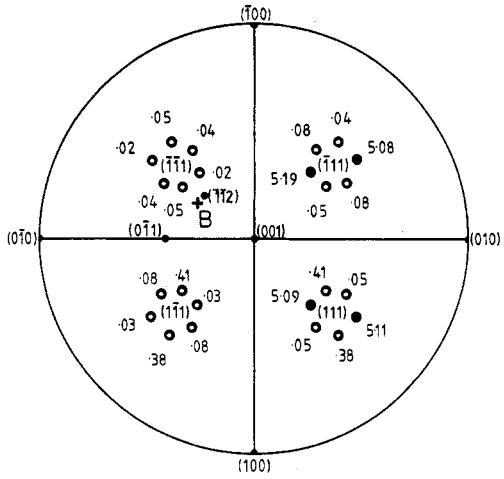

Figure 2. Stereogram showing, as circles, the directions of magnetic satellites around the four {111}-type directions in the upper half-space. In the experiment, the vertical direction was close to $(\bar{1}\bar{1}2)$ and the magnetic field (+) was applied 5° from that direction. The satellites favoured in that field are shown as full circles. The numbers give the ratios between the intensities of the satellites when cooled through T_N to 1.6 K with and without a field of 1 *T* applied. The satellites near the (111) direction were measured about the $(\frac{3}{2}, -\frac{3}{2}, \frac{1}{2})$ reciprocal lattice point, those near $(\bar{1}11)$ around $(\frac{5}{2}, -\frac{1}{2}, \frac{3}{2})$, $(\bar{1}, \bar{1}, 1)$ around $(\frac{5}{2}, \frac{1}{2}, \frac{3}{2})$ and $(1\bar{1}1)$ around $(\frac{3}{2}, \frac{1}{2}, \frac{3}{2})$.

was obtained by assuming that the moments associated with any hexagon of satellites lie along that {111} direction which passes through the centre of the hexagonal pattern [3, 4]. It was further assumed that the structure was single-*q*, so that a single domain would give rise to just two of the six satellites in a hexagon. To describe a domain of such a structure, it is convenient first to consider a type-II antiferromagnet [5] which has the wavevector $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$—that is, a unit cell doubled in all three directions. Inside the doubled unit cell, the moments lie parallel or antiparallel to the (111) direction. A pair of satellites at $(\pm\delta, \mp\delta, 0)$ from $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is then generated if this type-II antiferromagnet is also subject to a long-period modulation along the $(1\bar{1}0)$ direction. The other satellites in the hexagon are generated by domains with modulations along $(01\bar{1})$ and $(10\bar{1})$, which like $(1\bar{1}0)$ are perpendicular to (111).

Shortly after the publication of this description of the magnetic structure of $CeAl_2$, it was proposed that the three {110} modulations in a hexagon might be coupled together in a triple-*q* structure [6]. This was disproved by Barbara *et al* [7] who showed that the application of quite moderate uniaxial stress caused some members of the hexagon to increase in intensity but others to decrease. Thus the modulation vectors within a single hexagon are not coupled together in a triple-*q* state. However, in that experiment not all modulation vectors were observed, so [7] did *not* rule out *all* possible couplings between different modulation vectors. In view of this, and the important conclusions

which have been drawn from the supposed single-q modulated state of $CeAl_2$, we have re-investigated the matter, using a magnetic field instead of uniaxial stress to make different domain orientations inequivalent.

The $CeAl_2$ crystal used in this study was grown by the Czochralski method from a stoichiometric melt held in a tungsten crucible under purified argon at 2 bar. High purity start materials were used†. An approximately cylindrical specimen with length and diameter of about 12 mm was spark-cut from the boule and then etched in dilute HCl. Elastic neutron diffraction measurements were performed at the Institut Laue–Langevin using the D10 diffractometer operating at 2.36 Å. The detector was preceded by a pyrolytic graphite analyser to reduce background. The sample was mounted inside a small vertical-field cryomagnet which was set on goniometer arcs so that magnet and sample together could be tipped away from the vertical by up to 20°. In this way, satellites arising from a *full set* of modulation vectors could be brought into the horizontal scattering plane, and their intensities observed.

The initial orientation that we chose for the magnetic field is described by the stereographic projection shown in figure 2. In this diagram, the 24 satellites around the four {111}-type directions in the upper half-space are denoted by circles. The magnetic field of 1 T was applied some 5° from the $(\bar{1}, \bar{1}, 2)$ direction, so that it was at a different angle to each of the {111} directions, and would make them inequivalent. The value of this field was chosen to be much less than the approximately 5 T value that causes the magnetic ordering to change [4]: it depresses T_N by less than 0.1 K. Thus, satellite intensity changes would be due to the field favouring particular domain orientations. In zero field, all of the satellites had similar intensities, but when the specimen was cooled through T_N to 1.6 K in a field of 1 T, these intensities were markedly altered. Note in figure 2 that there was a big increase in the intensity of one pair of satellites about the (111) direction, which is perpendicular to the field—this is the usual response of an antiferromagnet: a domain which has a moment orientation perpendicular to the field is preferentially formed on cooling through T_N. However, the intensity of another pair of satellites is also *increased* by essentially the same factor. These satellites are around the $(\bar{1}\,1\,1)$ direction that is at an angle 67° to the field. All other satellites are decreased in intensity. The only plausible explanation of this is that the magnetic structure is *double-q*, with the two favoured modulations and moment directions coupled together and present simultaneously within a single domain. It is notable that the favoured pairs share the same modulation vector, $(0, \delta, \delta)$, about their respective $\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$ centres. The effect of the field may be summarized as follows: it selects that *pair* of moment directions which are most perpendicular to the field; the favoured modulation vector is the one which is common to the selected moment directions. A closer study of figure 2 will show that the intensities of satellites due to less-favoured domain orientations are coupled together in the same way. Finally, we note that with a double-q state, there are only six possible domain orientations instead of the twelve of the single-q model. As expected, the intensity due to the favoured double-q domain in figure 2 is increased by a factor approaching six.

We needed the unsymmetrical field direction of figure 2 to make all moment directions inequivalent and thereby prove the existence of this double-q state. However, we were able to prepare it in a much purer single-domain form, using the field orientation shown in figure 3. On cooling through T_N in 1 T, the intensities of the satellites indicated that more than 96% of the specimen was in the preferred domain orientation. When the

† Ce purchased from Ames Lab. Total metallic impurities, 35 ppma; interstitials, 420 ppma; other rare earths, 4 ppma. Al 59s supplied by Goodfellow Metals.

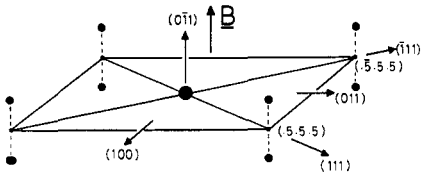

Figure 3. Satellites from a single domain of the magnetic structure, and the magnetic field direction which favours that domain.

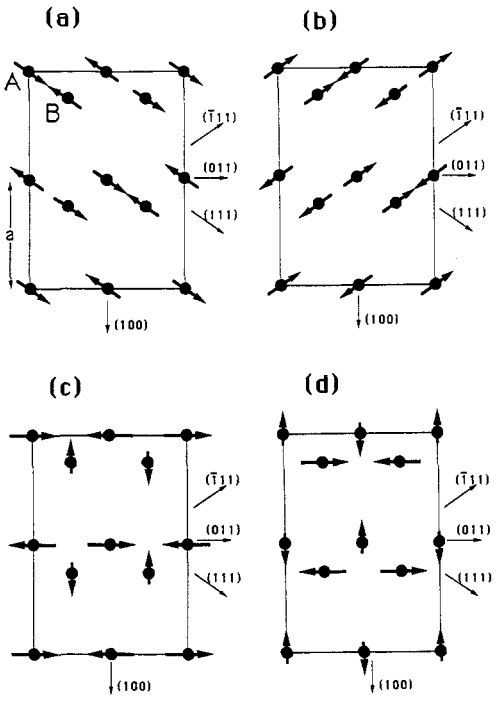

Figure 4. Representation of Ce ion positions and moment directions in a $(0, \bar{1}, 1)$ plane of $CeAl_2$ when magnetically ordered with the modulation vector perpendicular to the page. The repeat distance a of the chemical unit cell is shown. (a) Single-q magnetic structure with the moment direction along (111); (b) single-q magnetic structure with the moment direction along $(\bar{1}, 1, 1)$; (c) the superposition (a) + (b); (d) the superposition (b) − (a).

field was reduced to zero at 1.6 K, more than 75% of the specimen remained in that domain orientation. At low fields, stress due to differential thermal contraction between the sample and the holder could, by magnetoelastic interaction, overcome the aligning effects of the field. We believe that this is the cause of the minor domain repopulation.

It remains to interpret our observations in terms of a microscopic arrangement of magnetic moments. This may be aided by reference to figure 4, which shows the Ce ions in a single $(0, \bar{1}, 1)$ plane of the $CeAl_2$ structure (which has two FCC sublattices of Ce ions with origins at (000) and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ in the unit cell). The relative directions of the moments on the two sublattices are given by Barbara *et al* [4]. Since the zero-field satellite intensities that we observed are not inconsistent with this magnetic structure, we take it

as our starting point. For a single-q structure with moments along (111) and modulation perpendicular to the $(0, \bar{1}, 1)$ plane, the moment directions are as given in figure 4(a). A single-q structure with moments along $(\bar{1}, 1, 1)$ is represented in figure 4(b). In figure 4(c), these two single-q structures are superposed in phase, and in 4(d) in antiphase.

We see that if the observed double-q state is formed as in 4(c) or (d) (which differ only by interchange of the two Ce sublattices) then the moments at the Ce sites point along (011) and (100) directions, even though the components of this structure have moments only along {111}-type directions. If this is the true structure of $CeAl_2$, this pattern would be modulated in *amplitude* along the $(0, \bar{1}, 1)$ direction perpendicular to the page, and so would contain sites having zero moment.

An alternative possibility is that the two components, 4(a) and (b), are added in quadrature. In this case, the magnitudes of the moments would be zero nowhere, and their directions would rotate from 4(a) to (c) to (b) to (d), forming spirals with axes along the $(0, \bar{1}, 1)$ direction. Note, however, that the overall structure would be a *non-chiral* spiral, as evidenced by the fact that the moments at points A and B rotate in opposite senses.

Because there is no interference between the diffraction due to the two components of this double-q structure, it is not possible *by this experiment alone* to determine the phase with which the double-q components are added. However, measurements [8] of the high-field magnetization of single-crystal $CeAl_2$ allow us to make a clear decision. These measurements show a small but significant anisotropy (about 10%) in the magnetization: above T_N, where the results are not complicated by magnetic ordering, (100) is the 'hard' direction, with (110) intermediate and (111) the 'easy' direction. It is therefore highly unlikely that $CeAl_2$ orders in the non-spiral double-q state, since in that structure the moments never point along the easy direction. In a spiral state, the moments rotate among all three directions, which exacts a smaller penalty in anisotropy energy. Another factor favouring a spiral state is the increase in exchange interactions due to the absence of sites with zero moment.

A further argument for the spiral structure is the extreme weakness of the harmonics [4]. No longer is it necessary to postulate a non-magnetic ground state in order to explain the absence of 'squaring up' in a modulated structure; instead, the weakness of the harmonics is readily explained by the fairly constant moment value in a spiral structure. It should, however, be pointed out that the spirals in our model are elliptical (ratio of principal axes = $\sqrt{2}$) because the two-component moments are not exactly at right angles. Also, we have observed weak harmonics ($\lesssim 0.001$ of the fundamental at 1.6 K) which we believe arise from the anisotropy within the plane in which the moments rotate. A value for the average moment in the spiral may be derived from the neutron diffraction results of [4]. The RMS amplitude in our model is $2^{-1/2}$ times the amplitude of the modulated moment in the single-q model, i.e. $0.89/\sqrt{2} = 0.63\ \mu_B$. It follows that the site moments vary in the range ~ 0.53 to $0.75\ \mu_B$. For comparison, an isolated Γ_7 doublet state of Ce^{3+} has a magnetic moment of $0.71\ \mu_B$, while in a simple mean-field model, the exchange field admixture of the Γ_8 quartet would give an ordered moment of $\sim 0.86\ \mu_B$. The reduction of the maximum moment from this value may indicate a small degree of Kondo compensation of the moment, but it is probably not worth speculating further until more precise experimental data are available.

In conclusion, we have shown that the magnetic ordering of $CeAl_2$ is double-q and that the most natural interpretation of our results is a non-chiral spiral magnetic structure. In our new model, the ordered magnetic moment does not go to zero on any Ce site, so there is no longer any need to postulate the existence of a non-magnetic Kondo ground state for the Ce ions in this material.

We acknowledge the financial support of the SERC for this research, and the advice and assistance of the staff at the Institut Laue–Langevin, particularly Th Brueckel and R Chagnon.

References

[1] Buschow K H J and van Daal H J 1969 *Phys. Rev. Lett.* **23** 408
Cornut B and Coqblin B 1972 *Phys. Rev.* B **5** 4541
[2] Bredl C D, Steglich F and Schotte K D 1979 *Z. Phys.* B **29** 327
[3] Barbara B, Boucherle J X, Buevoz J L, Rossignol M F and Schweitzer J 1977 *Solid State Commun.* **24** 481
[4] Barbara B, Rossignol M F, Boucherle J X, Schweitzer J and Buevoz J 1979 *J. Appl. Phys.* **50** 2300
[5] Rossat-Mignod J 1979 *J. Physique Coll.* **40** C 5 95
[6] Shapiro S M, Gurewitz E, Parks R D and Kupferberg L D 1979 *Phys. Rev. Lett.* **43** 1748
[7] Barbara B, Rossignol M F, Boucherle J X and Vettier C 1980 *Phys. Rev. Lett.* **45** 938
[8] Barbara B, Rossignol M F, Purwins H G and Walker E 1975 *Solid State Commun.* **17** 1525