Quasimagnetic ordering of planar spins in a random anisotropy system: $Dy(As_{0.35}V_{0.65})O_4$

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Distortions due to random As/V substitutions in $Dy(As_{0.35}V_{0.65})O_4$ break local tetragonal symmetry and induce a uniaxial moment parallel to one or the other basal plane axis. This system thus provides an ideal random magnetic anisotropy antiferromagnet with equivalent competing axes and no dilution of the magnetic ions. Quasielastic neutron-scattering experiments of antiferromagnetic ordering at (100) showed a broad peak below 8 K with modest temperature dependence and a narrow peak that grew rapidly below 1.6 K. The narrow peak implies long range (800 Å) spin correlations but is never resolution limited, ruling out a conventional magnetic transition. These results are qualitatively consistent with predictions of an unusual transition at the lower critical dimension for the random anisotropy model. [S0163-1829(96)51930-2]

The nature of ordered phases in magnetic systems with random uniaxial anisotropy has been studied intensively for many years.[1,2] The random magnetic anisotropy (RMA) model was originally introduced[3] to account for spin glass and ferromagnetic phases in amorphous magnetic alloys. The standard Hamiltonian is

$$H=-J\sum_{\langle ij\rangle}\sum_{\alpha=1}^{m}S_i^{\alpha}S_j^{\alpha}-D\sum_i\left(\sum_{\alpha=1}^{m}(\hat{\mathbf{n}}_i^{\alpha}S_i^{\alpha})^2-1\right), \quad (1)$$

where each S_i is an m-component spin, the $\hat{\mathbf{n}}_i$ are random m-component unit vectors, and J and D are constants. While research on these materials as well as related systems has established the important role of RMA on their magnetic properties, there is still considerable uncertainty on many basic issues.[1]

Much of the experimental work on RMA systems has been devoted to amorphous metallic alloys whose composition includes magnetic (iron group or rare earth) and other atoms.[2] Such systems inherently combine random exchange interactions with random orientations of the anisotropy axes, and their suitability for testing predictions based on RMA models of certain aspects of magnetic ordering may be questioned. RMA effects have also been explored extensively in several mixed magnetic insulating compounds, of which $Fe_{1-x}Co_xCl_2$ is a good example.[4] In this case the crystal fields at the $3d$ ion sites act on Fe spins to give an easy axis parallel to the hexagonal unit cell axis, and on Co spins to favor alignment perpendicular to this axis. Although in this case the crystalline structure ensures that the spin-spin separations remain essentially uniform, the competing orientations are not equivalent, and the Fe-Fe, Co-Co, and Fe-Co exchange interactions may be quite different. It may also be difficult to get the Co concentration just right to allow exploration of the interesting multicritical point where Fe and Co spins order simultaneously.[4]

In this article we present results of an investigation by neutron scattering of magnetic ordering in a nearly ideal RMA system, $Dy(As_{0.35}V_{0.65})O_4$. This compound has a fortuitous combination of properties that provide a nearly ideal RMA system. The magnetic Dy ions are neither mixed nor dispersed, instead the random strains associated with As/V substitutions generate random uniaxial anisotropy at Dy sites. Moreover the Dy moments lie in the basal plane of the tetragonal unit cells, so the spin and lattice dimensionalities are $m=2$ and $d=3$, respectively. Theoretical investigations of this case have proposed that $d=3$ is the lower critical dimension for magnetic ordering,[2] and that a transition with subtle properties occurs.[5]

The key property in defining the RMA behavior of this system is a strong coupling between the Dy ground states and orthorhombic distortions in the isomorphous tetragonal compounds $DyVO_4$ and $DyAsO_4$.[6] This coupling is sufficient to drive cooperative Jahn-Teller phase transitions in pure $DyVO_4$ and $DyAsO_4$ at about 14 and 11 K, respectively. The Dy magnetic moments are dramatically affected by this orthorhombic transition: the g factors[7] go from $g_a=g_b\approx 10$ to $g_a\approx 19$, $g_b\approx 0$ in the orthorhombic phase, where a is the shorter of the orthorhombic basal plane axes. The g factor parallel to the tetragonal axis, g_c, remains unchanged at a value near unity, so that the magnetic spins go from planar to uniaxial as a result of the orthorhombic transition. The magnetic transition in $DyVO_4$ and $DyAsO_4$ is thus an Ising antiferromagnetic transition, occurring at 3.0 and 2.5 K, respectively.[7]

If As ions are introduced substitutionally and randomly for V ions, the As/V size difference will result in orthorhombic distortions with random orientations at each Dy site. This amounts to a random *strain* field that will inhibit the cooperative tetragonal-orthorhombic transition.[8] At the same time these distortions give a random uniaxial anisotropy field at each Dy site that potentially would affect the antiferromagnetic ordering at lower temperatures. For relatively small As doping levels, $x<0.2$ approximately, the orthorhombic transition still occurs, although at a reduced temperature. In this case the cooperative distortion will overwhelm the random distortions and all the Dy spins (in a particular structural domain) will have the same lattice and anisotropy axis. The

antiferromagnetic transition is thus essentially the same Ising transition as in the pure compound.[8] However, for larger x the orthorhombic transition is suppressed, the crystal remains tetragonal on average, and the Dy spins will respond to the random anisotropy fields. The RMA model should thus apply to antiferromagnetic ordering in this system. Since the Dy spins remain at full concentration at regular lattice sites it should be possible to explore intrinsic RMA behavior without the complexities arising from two spin species with different interactions. Some years ago the system $Dy(P_xV_{1-x})O_4$ was studied in the context of the RMA model[9] but this is a more complex system. In $DyPO_4$ the Dy wave functions are quite different from those in $DyVO_4$ and $DyAsO_4$, and magnetic ordering occurs parallel to the c axis rather than in the basal plane. Moreover, based on what is now known about the behavior[8] of $Dy(As_xV_{1-x})O_4$, we expect that for any significant P concentrations the tetragonal-orthorhombic transition will be suppressed, so that the Dy spins can align parallel to the c axis or either a axis depending on the local environment. The spin dimensionality is thus 3, not 2, with the c axis inequivalent to the other two.

Theoretical investigations of the RMA model have addressed the issues of the existence and nature of a transition from the paramagnetic phase to a conventional long-range ordered phase or to a spin glass phase. There is substantial evidence[1,2] that for the physically important cases of spin dimensionalities $m=2,3$ in a three-dimensional lattice conventional long-range order does not occur. For $m=2$ there is evidence from computer simulations[5,10] for a phase transition (i.e., diverging susceptibility) at a nonzero temperature, but not for $m=3$. The transition for $m=2$, however, has been found not to have long-range order but only power-law spin correlations.[5,10] Experimental investigations that might confirm these results and provide physical insight on the nature of this transition would clearly be valuable.

The sample crystal, of dimensions $2\times4\times7$ mm, was grown by flux methods at the Clarendon Laboratory, University of Oxford,[11] and mounted with c axis vertical in a pumped helium cryostat at the N5 spectrometer at Chalk River. The neutron-scattering experiments examined the development of antiferromagnetic ordering at (100), an intense magnetic peak in experiments on pure $DyVO_4$.[12] A quasielastic (no analyzer) configuration was chosen, with the collimation initially set rather coarse (50′ before and 90′ after the sample) to give good counting rates for broad weak peaks characteristic of short-range ordering. The estimated full widths at half maximum of the resolution ellipse were 0.028, 0.0058, and 0.091 r.l.u. in the parallel, perpendicular, and out-of-plane directions, respectively. The Si (111) monochromator was set for a neutron wavelength of 2.37 Å, and graphite filters were inserted before and after the sample to reduce half-wavelength scattering.

At most temperatures radial and transverse scans through (100) showed both a broad and a sharp peak, most clearly distinguishable (Fig. 1) in transverse scans where the resolution was higher. Since their widths differed by almost two orders of magnitude (see high resolution data of Fig. 3), they could be fitted most efficiently and consistently by separately fitting data for the narrow peak and the wings of the broad peak. The broad peak was visible up to 8 K. The transverse width (Fig. 2) is roughly constant down to 2.5 K, but it

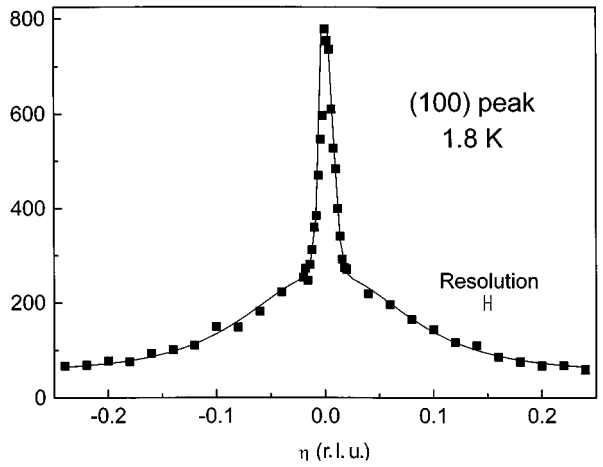

FIG. 1. Transverse scan at 1.8 K showing the broad and narrow (100) peaks. The broad peak is fitted to a Lorentzian-squared function.

decreases somewhat at lower temperatures. The radial width behaves similarly, but statistics for it are poorer. The intensity of the broad peak, as given by the product of peak amplitude and radial and transverse widths, increases slowly down to 2 K and more rapidly at lower temperatures. The line shape was fitted well by a Lorentzian-squared function (see Fig. 1) at all temperatures, although only at the lowest temperatures were the statistics good enough to rule out Lorentzian or Gaussian functions.

Investigation of the narrow (100) peak was hindered by some residual feedthrough from (200) Bragg scattering, and by significant sample mosaic broadening and structure. The latter consisted of three main peaks and other structure extending over an angle of 60′. An intrinsic (not feedthrough) narrow peak appears below 2 K and grows rapidly below 1.6 K, suggesting antiferromagnetic ordering. In order to examine changes in the line shape of this narrow peak the collimation before and after the sample was tightened to 20′ and 60′, respectively, giving resolution widths of 0.018 and 0.0033 r.l.u. parallel and perpendicular to the scattering wave vector. To extract the widths associated with magnetic scat-

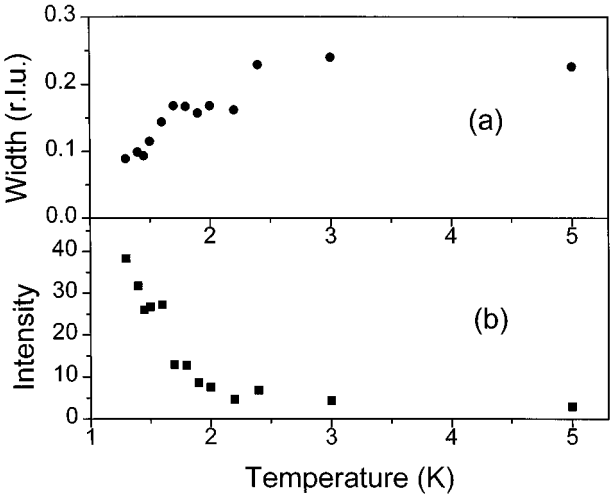

FIG. 2. Temperature dependence of the (a) width and (b) intensity of the broad (100) peak.

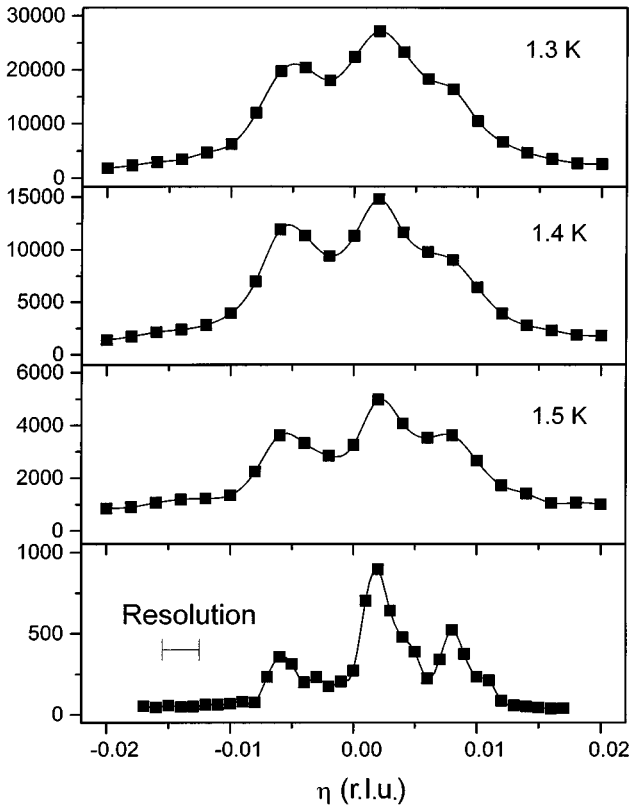

FIG. 3. High-resolution scans through the narrow magnetic (100) peak at low temperatures. The lowest panel is a Bragg peak showing the sample mosaic. Lines through the points are guides to the eye.

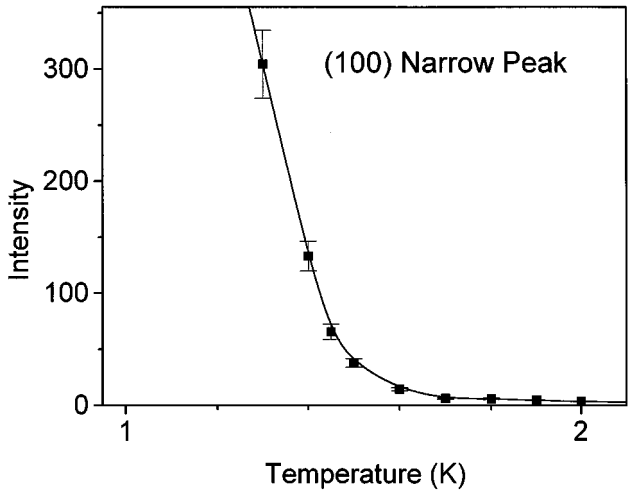

FIG. 4. Intensity (arbitrary units) of main component of narrow line at low temperatures, showing rapid growth of antiferromagnetic order. The line through the points is a guide to the eye.

tering, the main peaks were fitted to three Lorentzian functions with equal widths. It was found that the three peaks showed slightly different temperature dependences during magnetic ordering; accordingly, only data derived from fits to the main central peak will be presented.

Close examination of the narrow peak line shapes below 1.6 K (Fig. 3) shows a modest but definite increase in linewidth accompanying the growth in intensity at lower temperatures. The lowest panel in Fig. 3 gives the line shape when limited only by the sample mosaic: it represents a scan at 2 K where the magnetic scattering is negligible and where the graphite filters have been removed to allow feedthrough from (200) Bragg scattering. It is clear from these data that the magnetic peaks are broadened at all the temperatures shown, and that the broadening increases at lower temperatures. (Line shapes at 1.6 K and above cannot be compared directly because they were taken with coarser collimation.) Figure 4 shows the intensity of the central component of the narrow line as a function of temperature. The residual feedthrough has not been subtracted, and amounts to about unity on the intensity scale shown. The growth in intensity suggests a magnetic transition, although there is no distinct discontinuity, perhaps due to sample inhomogeneities.

The growth of spin correlations in a disordered system is commonly characterized by slow equilibration due to a range of energy barriers. In this experiment the magnetic scattering showed conspicuous time dependence relative to the time scale of a typical scan through the (100) peak. We therefore adopted the procedure, after changing the sample temperature, of scanning repeatedly through the peak, and taking as equilibrium data those scans for which the counts had stabilized within statistical fluctuations. At the higher temperatures where the scattering is broad and weak, counting times of several minutes per point are required and we can only probe time scales of a half hour or longer. Above 3 K we could detect no time dependence, and infer that equilibration times are shorter than 30 minutes. At very low temperatures counting rates are much higher, but equilibration is much slower. Our data suggest that equilibration times increase smoothly from about one hour at 2.4 K to 10 hours at 1.5 K but, interestingly, do not seem to increase significantly for further reductions in temperature down to 1.3 K, implying that it should be possible to make equilibrium measurements at even lower temperatures in this system.

A number of conclusions can be drawn from this study, although important questions still remain. The rapid growth in the (100) peak below 1.6 K (Fig. 4) suggests an antiferromagnetic phase transition, but such a description requires caution in random systems where there are theoretical and experimental problems in identifying a phase transition. In neutron experiments the usual signature of a transition is the narrowing of the diffuse magnetic scattering to a resolution-limited peak followed by the rapid growth of a resolution-limited peak due to coherent magnetic scattering as the temperature is reduced. In the present case the broad (100) peak narrows only slightly as the temperature decreases, and even at 1.3 K its width implies spin correlations extending over only 2 or 3 unit cells. The narrow peak begins to appear below 2 K but as far as can be determined under the experimental conditions it always has an intrinsic width. In analysing its width we assumed a Lorentzian line shape, and hence exponential spin correlations, but the sample mosaic structure prohibits a reliable determination of the correlation function. Nevertheless the growth of the narrow peak below 1.6 K and the implied range of spin correlations of 800 Å are sufficiently characteristic of a transition that we may refer to this as quasi-antiferromagnetic ordering.

Of particular interest in these results is the origin of the broad peak and its relation to the narrow peak. Somewhat similar peaks have been associated with ''second length

scale'' phenomena in a number of ordered systems.[13] The relatively weak temperature variation of the width and intensity of the broad peak in this system suggests that it originates from spins in small volumes, typically only a few unit cells in size, where the environment is strongly disordered. There is evidence, however, that the spins associated with the broad peak are not a separate community, e.g., spins close to the surface or to extended crystal defects, but are able to interact with the spins that order at 1.6 K. First, the equilibration times for the broad and narrow peaks appear to be the same, implying that the two sets of spins are in good thermal contact. Second, the observations that the intensity of the broad peak grows significantly over the range of temperature in which the narrow peak grows rapidly, and that the broad peak narrows as the narrow peak broadens at the lowest temperatures, suggest some mutual influence between the two sets of spins. At most temperatures studied, the intensity associated with the broad peak, and hence the number of spins, is much greater than for the narrow peak. At the lowest temperature reached, 1.3 K, the narrow peak has grown so that it dominates the scan, and if the trend of Fig. 4 continues to lower temperatures, the broad peak will be essentially unobservable. Thus the distinction between the two spin environments no longer applies and a description in terms of a bulk phase transition appears justified.

Numerical simulations[5,10] that predict a phase transition for the $m=2$, $d=3$ RMA model also give an estimate of the critical temperature T_c, and it would be of interest to compare it with our experimental value of 1.6 K. However, we cannot simply say that T_c has been reduced from its value in the absence of RMA of 2.8 K (a weighted average[7] of T_c for pure $DyVO_4$ and $DyAsO_4$) because the latter value comes from Ising spins in the orthorhombic pure crystals. The comparison should be instead with the antiferromagnetic transition temperature in a crystal with no RMA that remains tetragonal so that the spins retain planar symmetry. This datum is not available experimentally, nor can it be estimated from the value of J deduced from the Ising transition that actually occurs, since the orthorhombic transition alters the magnetic wave functions, the g factors, and hence the spin-spin interactions. However an alternative approach is possible, based on the strong anisotropy limit[5] of Eq. (1), $D/J\rightarrow\infty$,

$$H_{\infty}=-J\sum_{\langle ij\rangle}(\hat{\mathbf{n}}_i\cdot\hat{\mathbf{n}}_j)S_iS_j\,, \tag{2}$$

where each S_i is now an Ising variable. This simpler Hamiltonian is believed to retain the essential physics of the planar RMA model and is the basis of much of the computational research.[1] In our system the fact that the strain-induced ion-ion couplings are stronger than the magnetic interactions suggests that this limit is appropriate. We therefore assume that the constant J is the same for the tetragonal case with strong RMA and the orthorhombic case without RMA, giving a reduction of approximately $1.6/2.8=0.57$. Fisch[5,10] estimates $T_c=1.94J$ for strong RMA in the simple cubic lattice, and this can be compared to $T_c=4.5J$[14] without RMA, giving a predicted reduction of $1.94/4.5=0.43$. Hence the observed reduction in T_c is consistent with the expected value, considering all the uncertainties in the comparison.

In summary, neutron-scattering experiments in a nearly ideal RMA system for the case $m=2$ and $d=3$ show long- but finite-range antiferromagnetic spin correlations. The data are consistent with predictions of quasimagnetic ordering corresponding to the lower critical dimension.

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[1] Y. Y. Goldschmidt, in *Recent Progress in Random Magnets*, edited by D. H. Ryan (World Scientific, Singapore, 1992).
[2] D. J. Sellmyer and M. J. O'Shea, in *Recent Progress in Random Magnets* (Ref. 1).
[3] R. Harris, M. Plischke, and M. J. Zuckermann, Phys. Rev. Lett. **31**, 160 (1973).
[4] P. Wong, P. M. Horn, R. J. Birgeneau, and G. Shirane, Phys. Rev. B **27**, 428 (1983).
[5] R. Fisch, Phys. Rev. Lett. **66**, 2041 (1991).
[6] G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. **38**, 1 (1975).
[7] A. Kasten, Z. Phys. B **38**, 65 (1980).
[8] D. R. Taylor, K. A. Reza, and J. T. Graham, Phys. Rev. B **52**, 7108 (1995), and references therein.
[9] P. Kettler *et al.*, Phys. Rev. Lett. **47**, 1329 (1981).
[10] R. Fisch, Phys. Rev. B **51**, 11 507 (1995).
[11] B. M. Wanklyn, B. E. Watts, and B. J. Garrard, Mater. Res. Bull. **19**, 825 (1984).
[12] G. Will and W. Schäfer, J. Phys. C **4**, 811 (1972).
[13] P. M. Gehring *et al.*, Phys. Rev. Lett. **71**, 1087 (1993).
[14] A. M. Ferrenberg and D. P. Landau, Phys. Rev. B **44**, 5081 (1991).