Ordering Effects in the Random-Anisotropy System $Dy(P_{1-x}V_x)O_4$

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Measurements are reported of the magnetization, magnetic ordering, and optical absorption of mixed single crystals of $Dy(P_{1-x}V_x)O_4$. This compound is shown to be a good example of a system with random spin anisotropy. In contrast to the results on $Fe_{1-x}Co_xCl_2$, no tetracritical point is found, and long-range magnetic order is destroyed by rather small concentrations of the minority component. These results agree with recent theories on random-anisotropy systems.

In recent years much interest has been shown in systems with any kind of randomness in their microscopic structure. Special attention was given to the case of a mixture of two systems having similar structures, but different types of magnetic ordering.[1-3] In these systems, under certain conditions a new phase is predicted, which displays the ordering of neither of the original types but nevertheless exhibits long-range order (LRO). If this new phase exists, it is predicted to be separated by second-order transition lines[2] and to exhibit a "decoupled tetracritical point." On the other hand, random anisotropy is predicted[4] to raise the critical dimension of systems by two and thus to destroy LRO in any real system with spin dimensionality ≥ 2. Experiments on such systems were reported,[5-7] and were found to be in agreement with the theories with regard to the existence of a tetracritical point, but did not give a clear indication about the nature of the transition lines. Recently a new analysis of the properties of $Fe_{1-x}Co_xCl_2$ took place,[8] which showed that this tetracritical point is not decoupled, but that any ordered parameter is influenced by the ordering of the "majority" component. In this system, a competing spin anisotropy is realized by two different magnetic ions, randomly distributed on identical sites in the lattice. We report measurements on the system $Dy(P_{1-x}V_x)O_4$, in which a random spin anisotropy is obtained by having identical magnetic ions in a surrounding which induces different properties at each ion site. Our results seem to suggest that in this

system the nature of the phase transition is influenced already by small amounts of the minority component, without obtaining a tetracritical point. This is consistent with the random-anisotropy model, in which LRO is destroyed by the randomness.

We investigated mixed crystals of the system $Dy(P_{1-x}V_x)O_4$ and here report measurements of magnetization in applied fields, of spontaneous magnetic ordering, and of optical absorption on the mixed crystals. The pure $DyPO_4$ and $DyVO_4$ crystallize in the tetragonal zircon structure, space group $D_{4h}{}^{19}$ ($I4_1/amd$), with slightly different lattice constants.[9,10] At 14 K there is a structural phase transition in $DyVO_4$, in which a Jahn-Teller distortion lowers the symmetry to orthorhombic.[11] In the lattice, the Dy^{3+} ions are surrounded by six PO_4 or VO_4 tetrahedra, which determine the crystal field (CF) at the site of the Dy ions. The CF acts on the level splitting in the Dy ion and yields different ground states in the different pure substances.[12,13] This results in different directions of the easy axis for the magnetic moments, which is the c axis in $DyPO_4$ and the a axis in $DyVO_4$. Therefore, a mixture of $DyPO_4$ and $DyVO_4$ creates spin anisotropies which are random in size and direction at each individual Dy- ion site. At 3.4 K in $DyPO_4$ and at 3.0 K in $DyVO_4$ the spins begin to order in antiferromagnetic arrangements parallel to their respective easy axes.[9,10]

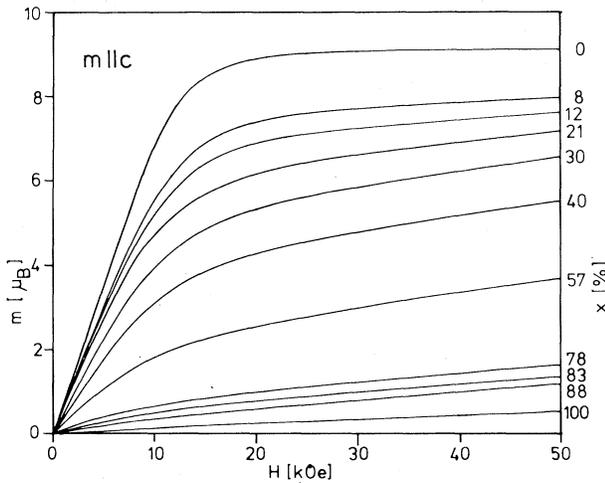Mixed crystals of this system were flux grown at Clarendon Laboratory, Oxford. These crys-

FIG. 1. Magnetization m of $Dy(P_{1-x}V_x)O_4$ at $T = 4.2$ K as a function of applied field. Curves are labeled by the concentration parameter x. The orientation of the field is parallel to c axis.

tals have typical dimensions of $1 \times 1 \times 5$ mm^3 along the a, b, and c axis, respectively. The lattice constants were determined by x-ray powder diffraction, and the concentration parameter x was determined by electron-probe microanalysis (EPMA) with an accuracy of $\pm 1\%$, and cross-checked by neutron activation analysis (NAA).

The magnetization has been measured with a vibrating sample magnetometer at Freie Universität, Berlin, with applied fields of $0 \leqslant H \leqslant 50$ kOe in the temperature range 2 K$\leqslant T \leqslant 300$ K. Results are shown in Figs. 1 and 2. Figure 1 shows the magnetic moment m per ion at $T = 4.2$ K versus the applied field for several concentrations and for the magnetic field directed parallel to the c axis. For $\vec{H} \perp \vec{c}$, similar results were obtained with the concentration scale reversed. Obviously m saturates at rather small fields for the pure substances only, while in the mixed samples m varies with field over the entire field range, with a slope which is strongly concentration dependent. As a measure of the temperature and concentration dependence of the anisotropy, the magnetization M at 1 kOe was recorded with the field along both principal directions as a function of the temperature for several concentrations x. The ratio $M_\perp/M_\parallel$, plotted on a logarithmic scale, is shown in Fig. 2. It shows (a) the sharp decrease of anisotropy with increasing temperature in the pure substances and for small amounts of impurities and (b) the nearly perfect isotropy of samples with concentrations x of about 40%.
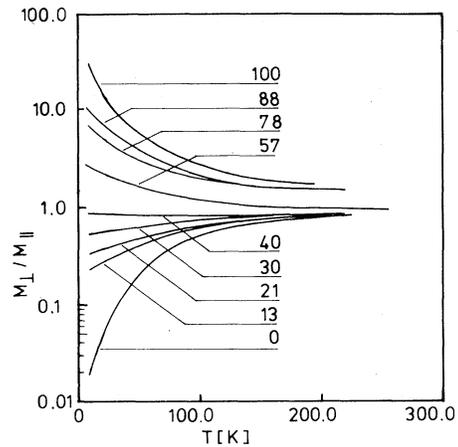

FIG. 2. Ratio of magnetizations in a and c directions $M_\perp/M_\parallel$ at $H = 1$ kOe as a function of temperature. Curves are labeled by the concentration parameter x.

The spontaneous magnetic ordering as a function of temperature was studied by neutron diffraction at the BERII reactor at Hahn-Meitner-Institut, Berlin. A ^{3}He cryostat was used to cool the samples down to 0.5 K. Purely magnetic reflections of (110) and (100) type, which are characteristic for the ordering type of $DyPO_4$ and $DyVO_4$, respectively, were recorded. Nuclear reflections of $(hk0)$ type were measured as well for normalization purposes. The normalization factor obtained from the nuclear reflections was then used to calculate the ordered magnetic moments from the observed intensities of the mag-
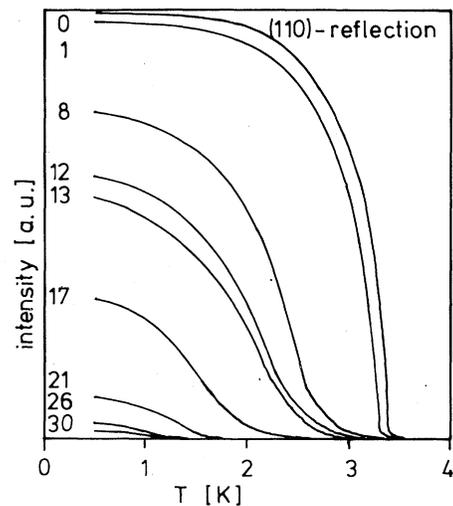

FIG. 3. Intensities of magnetic (110) reflections in $Dy(P_{1-x}V_x)O_4$ vs the temperature. Curves are labeled by the concentration parameter x.

netic reflections. These intensities were scaled using the ordered magnetic moment per ion at $T = 0.5$ K. In Fig. 3, the rescaled intensities of the (110) reflection as a function of the temperature are plotted. For the concentration range $78 \leq x \leq 100$, similar results for the (100) reflection were obtained. In samples which showed one type of ordering, the other type could never be detected. For concentrations of $x = 40\%$, 57%, and 65% neither ordering could be observed down to $T = 0.45$ K. Only the pure $DyPO_4$ and $DyVO_4$ show curves corresponding to proper phase transitions, while the mixed samples exhibit ordering effects without a sharp onset. From these curves, ordering temperatures were obtained by (a) a fit with a power law and by (b) determining the maximum of the derivative. The results are consistent and are given in Fig. 4. It shows a surprisingly steep decrease of ordering temperature with the admixture of the minority component.

The optical absorption measurements were done at 4.2 and 2 K with an 1-m Jarrel-Ash spectrograph at Technische Universität, Berlin. Spectra of the transition $^6H_{15/2}$ to $^6F_{5/2}$ taken at $H = 0$ kOe for several concentrations are presented in Fig. 5. They show the influence of the surroundings on the $4f$ shell of the Dy^{3+} ion. As a result of nonoptimal sample size, in some energy ranges the absorption is saturated, but nevertheless it shows the abrupt appearance of new lines upon the addition of small admixtures of V ions to a $DyPO_4$ ($x = 0$) sample and the disappearance of
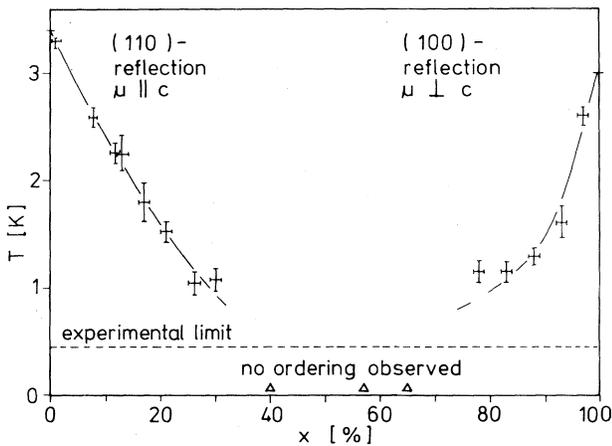
any sharp line further within the mixture. This indicates how strongly the electronic levels of the Dy ions are influenced by small changes in the CF.

In summary, for the spontaneous ordering we find a surprisingly steep decrease of both the ordering temperature and the effective magnetic moment with an increasing amount of admixture. No sample shows both types of ordering. In the concentration range of $30\% < x < 78\%$, no ordering is observed down to $T = 0.45$ K. This suggests that in $Dy(P_{1-x}V_x)O_4$ probably no mixed phase and no tetracritical point exists. Additionally, a considerable smearing of the transition is observed from the very beginning of the mixture, which cannot be explained by inhomogeneity in concentration, as the EPMA results show. Recent theories[4] claim that in systems with more than one spin component the LRO is destroyed for all realistic dimensions < 4 by random uniaxial anisotropy, as well as by random fields. For Ising systems, random fields are predicted[14] to increase the critical dimensionality to 3, but no predictions are made for the case of random anisotropies. In agreement with these predictions, the results of Wong et al.[8] show that for
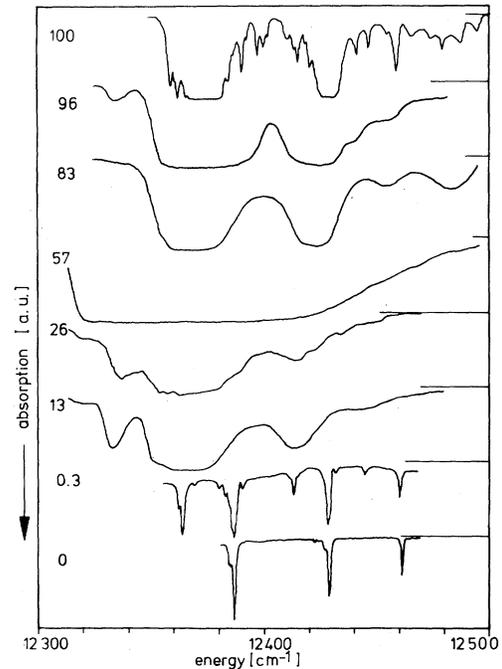

FIG. 4. Ordering temperatures vs concentration in $Dy(P_{1-x}V_x)O_4$. Solid line serves as guide for the eye only. Concentrations at which no ordering is found are marked by triangles.

FIG. 5. Optical absorption in Dy^{3+}, $^6H_{15/2}$ to $^6F_{5/2}$ transition, at $T = 4.2$ K and zero field as a function of energy in $Dy(P_{1-x}V_x)O_4$. Curves are labeled by the concentration parameter x.

random fields experimentally no significant dif-
ference between the continuous and the Ising case
is found. The magnetic properties of the Dy ions
are mainly influenced by the CF of their diamag-
netic neighbors. Taking only the six nearest
neighbor and next nearest neighbors into account,
fifteen configurations are possible, which result
in a random distribution of anisotropies of the
central Dy ion. Microscopically, the absorption
measurements show the appearance of new elec-
tronic levels, indicating a change in the CF split-
ting. In a magnetic field these lines show Zee-
man splittings,[15] which are quite different from
those of the lines due to the homogeneous sur-
roundings in the pure substances. Therefore,
while these are proper Ising systems, the spin
dimensionality in the mixed system remains
doubtful. This is consistent with the results of
the magnetization measurements, where the sub-
stitution of P by V in the mixture alters the mac-
roscopic anisotropy gradually from parallel to
normal to the c axis. Wong $et\ al.$[8] find in Co_{1-x}-
Fe_xCl_2, which is a mixture of an Ising and a X-Y
antiferromagnet, that the different partial sys-
tems order properly besides the tetracritical re-
gion. According to Fishman and Aharony,[2] this
is to be expected in the case of $mixed$ anisotro-
pies. Because in that case the moments are fixed
in direction on each ion type, random effects oc-
cur only in the vicinity of the tetracritical point
by cross terms in the Hamiltonian, which pro-
duce a local random field. In our system, which
we feel exhibits $random$ anisotropies over the en-
tire concentration range, the second-order tran-
sition is smeared from the very beginning of the
mixture, and LRO is suppressed, as expected.

[1]F. Matsubara and S. Inwashiro, J. Phys. Soc. Jpn.
42, 1529 (1977).
[2]S. Fishman and A. Aharony, Phys. Rev. B 18, 3507
(1978), 19, 3776 (1979), and 21, 280 (1980).
[3]P. A. Lindgård, Phys. Rev. B 14, 4074 (1976), and
16, 2168 (1977).
[4]A. Aharony and E. Pytte, Phys. Rev. Lett. 45, 1583
(1980).
[5]K. Katsumata, M. Kobayashi, and H. Yoshizawa,
Phys. Rev. Lett. 43, 960 (1979), and references there-
in.
[6]L. Bevaart, E. Frikkee, and L. J. de Jongh, Phys.
Rev. B 19, 4741 (1979).
[7]R. Geller, Ch. Klein, and K. Knorr, J. Magn. Magn.
Mater. 4, 199 (1977).
[8]P. Wong, P. M. Horn, R. J. Birgenau, C. R. Safinya,
and G. Shirane, Phys. Rev. Lett. 45, 1974 (1980).
[9]W. Scharenberg and G. Will, Int. J. Magn. 1, 277
(1971).
[10]G. Will and W. Schaefer, J. Phys. C 4, 811 (1971).
[11]J. B. Forsyth and C. F. Sampson, Phys. Lett. 36A,
223 (1971).
[12]D. W. Forester and W. A. Ferrando, Phys. Rev.
B 13, 3991 (1976).
[13]C. J. Ellis, K. A. Gehring, M. J. M. Leask, and
R. L. White, J. Phys. (Paris) 1, 1024 (1971).
[14]E. Pytte, Y. Imry, and D. Mukamel, Phys. Rev.
Lett. 46, 1173 (1981).
[15]P. Kettler and R. Germer, to be published.