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CHARACTERISTIC PROPERTIES OF (NEAR) HEISENBERG LAYER TYPE MAGNETIC CRYSTALS

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Résumé. — Les substances magnétiques susceptibles d'être étudiées par un modèle d'Heisenberg à deux dimensions sont passées en revue. On discute du point de vue expérimental de changement de phase dans un modèle d'Heisenberg appliqué à un réseau carré. Des résultats expérimentaux, on peut conclure d'une part à l'absence d'un changement de phase observée sur les mesures de chaleur spécifique, mais d'autre part que la susceptibilité diverge à température finie.

On montre aussi l'intérêt des aimants en couches non idéales. Des résultats expérimentaux sont présentés concernant:
- la réduction de spin dans les antiferromagnétiques;
- l'anisotropie de Rb₂NiF₄ et K₂NiF₄;
- la dépendance en température des largeurs de raie RMN dans K₂MnF₄ et KMnF₃.

Abstract. — The magnetic substances, available at this moment which approximate the theoretical Heisenberg model in two dimensions to a fair degree, are reviewed. The problem whether or not a phase transition exists for the quadratic Heisenberg magnet is discussed from an experimental point of view. It is concluded that experimental data at one hand point to the absence of a phase transition in the heat capacity but on the other hand they favour existence of a divergence in the susceptibility at a finite temperature.

The interest, also of non ideal layer type magnets, is illustrated. Experimental information is presented concerning (1) the spin reduction in antiferromagnets, (2) the anisotropy in Rb₂NiF₄ and K₂NiF₄ and (3) the temperature dependence of the N. M. R. line width in K₂MnF₄ and KMnF₃.

I. Introduction. — In theoretical studies on magnetic ordering one usually relies on rather simplified models. These simplifications concern for instance the dimensions of the system, which may be one, two or three and the type of interaction which is taken to be either fully anisotropic (Ising model) or completely isotropic (Heisenberg model, \( E_{xx} = -2JS_i S_j \)).

Whereas on first sight it may seem to be excluded to study simple magnetic systems experimentally, it nevertheless has been possible to find real substances which meet the requirements of the above theoretical models quite well. In this paper we review the situations for the two dimensional Heisenberg magnet (2 DH).

Figure 1 shows the crystal structure of Rb₂MnF₄. The two dimensional character will be clear from the figure; the cell can be described as consisting of layers MnF₃ separated by 2 layers KF. In addition it is quite important that for many compounds with this structure (K₂NiF₄, Rb₂FeF₄, Ca₂MnO₄, Rb₂MnCl₄, etc.) the interaction has the antiferromagnetic sign (see for a wide selection of references the papers of Lines [1] and Birgeneau [2] and many papers at this conference). Since neighbouring planes of magnetic ions are shifted over \( a/2, b/2 \) with respect to each other, the interaction between neighbouring magnetic layers cancels when the magnetic moments which are nearest neighbours within a plane become correlated. This means that at low temperatures the interaction in the third dimension will be that between next neighbouring planes and thus the interaction is orders of magnitude smaller than the intraplane interaction (ratio of relevant atomic distances \( d_3/d_2 \) is about 3).

The requirement of a 2 D lattice is somewhat better fulfilled for antiferromagnets with the Ba₂ZnF₄ structure, where the magnetic ion may be Mn, Ni or Fe [3].

As shown in figure 2 there is an extra layer of non magnetic atoms added (\( d_3/d_2 \approx 4 \)).

For the series of compounds with the general formula Cu₃(\( C_{H_{2n+1}}N_3 \))Cl₄ (\( n = 1...10 \)) the nearest neighbour interaction has the ferromagnetic sign [4, 5, 6]. The structure may be looked upon as
containing nearly quadratic layers of CuCl₂ separated by two layers of C₅H₂₅⁺,NH₃Cl. A similar series of compounds exists containing Br. The 2D character becomes more pronounced upon increasing n; the relevant copper-copper distances increase from $d_3/d_2 = 2$ to about 6.

Another interesting example is the free radical dipanisylnitrosyl (DPAN) investigated by Duffy [7] e.g. a. The crystal structure arranges the magnetic moments in layers with $d_3/d_2$ about 3. The dominant interaction has the antiferromagnetic sign. A variable two dimensional character is met in the manganous alkanoates [8], antiferromagnets with the general formula $(C_nH_{2n+1}COO)_2Mn$ ($n = 2...15$). Here $d_3/d_2$ goes up to 10. This series may be looked upon as derived from the well investigated [9, 10] layer compound Mn(COOH)₂·2H₂O for which the relevant interactions $J_3/J$ differ one order of magnitude already.

As a matter of fact also the anisotropy is important in deciding to which extent the compounds mentioned approximate the Heisenberg model. As a lower limit the dipolar interaction gives rise to an anisotropy for these far from cubic structures, which tends to orient the spins perpendicular to the layers for the 2D antiferromagnets and within the layer for ferromagnets. The corresponding anisotropies (and also the observed ones) are of the order $H_a/H_F = 10^{-2} - 10^{-3}$ for the a.f. fluorides, about $10^{-2}$ for DPAN and $10^{-3} - 10^{-4}$ and $10^{-5}$ for the ferromagnetic copper chlorides. It is noteworthy that for the latter compounds the anisotropy within the $a$-$b$ plane may be more than one order of magnitude smaller.

II. The phase transition. — The 2 DH-magnet has drawn considerable interest because for this system different theoretical descriptions lead to results which on first sight seem to be contradictory. At one hand it has been proved exactly [11] that the 2 DH-magnet and also the plane rotator in two dimensions [12] cannot have long range order at any $T > 0$. On the other hand exact series expansions for the susceptibility [13, 14] do give indications for a critical temperature (defined as that temperature where $\chi$ starts to diverge) which for the higher spin values are nearly as convincing in 2 as in 3 dimensions. Further theoretical investigations have shown that it is not impossible that a new type of «magnetic phase» exists which has no spontaneous magnetization but nevertheless infinite initial susceptibility. This combination may occur, if, crudely spoken, within a layer of magnetic spins the correlation of spins $S_R$ at distance $R$ with respect to a given spin $S_0$ decreases more slowly with $R$ than the number of spins at distance $R$ increases.

In the present paper we discuss the existence and the nature of the Stanley and Kaplan phase transition from an experimental point of view. Firstly we note that for many, if not all, experiments reported thus far the transition at $T_C (\chi$ or $\chi$ staggered $\rightarrow \infty$) has been from paramagnetism to ordinary long range order. This may be ascribed to the fact that for all these practical cases the deviations from the ideal system (as anisotropy, metamagnetism, interaction in the third dimension, finite size and finite demagnetizing factor, crystal imperfections) have been sufficiently large to induce long range order at a temperature higher than or equal to $T_C$ for the ideal case. Lines has suggested that for the a.f. fluorides the anisotropy determines $T_N$ and stabilizes the ordered phase; calculating $T_N$ by means of a Green function approximation Lines predicts $kT_D/J$ values as a function of $H_A/H_F$. If we define a critical anisotropy as that $H_A/H_F$ for which $T_N$ as calculated by Lines lies above that predicted from series expansions for $\chi$, this critical anisotropy depends on the spin value and varies between $H_A/H_F$ the order of $10^{-2}$ for $S = \infty$ to $H_A/H_F \approx 10^{-3}$ for $S = 1$.

The effect of $H_A$ becomes visible when comparing $K_2NiF_4$ and Rb₂NiF₄. The two isomorphous crystals have only slightly different $J$ values, whereas $H_A$ differs considerably. This may be seen from figure 3, which shows magnetization curves for $H$ parallel to the preferred direction (c-axis). The curves [18] show a sharp bend at the spin-flop fields of 180 and 350 kOe, respectively. Since the flop fields are proportional to $(H_AH_F)\frac{1}{4}$, the anisotropy affects a factor 4. From $\chi$ versus $T$ curves it can be derived that the ratio of the $kT_D/J$ values is 1.18 ± 0.04, in agreement with Lines prediction for the 2 DH antiferromagnet with small anisotropy, so that this experiment does not tell much about the ideal case. Correspondingly it is quite certain that for DPAN the anisotropy of $10^{-2}$ will be sufficiently large to permit the application of the R.-P. A. Green function calculation. Lines [17] predicts for this case $kT_D/J$ to be 0.3; indeed Duffy reports a weak anomaly in both $C_V$ and $\chi$-powder

![Fig. 2. — Crystal structure [3] of Ba₂ZnF₆. Comparison with K₂NiF₄ shows that in this structure the number of nonmagnetic layers in between two magnetic layers is increased.](image-url)
around $kT/J = 1.1$. However, it is remarkable that the anomaly in $C_V$ is rather unimportant. As shown in figure 4 the specific heat shows a broad maximum at temperatures around $kT/J = 1$ like the curves previously found for linear chain crystals for which there is no doubt that a phase transition is absent. The critical point in the specific heat (at $T = 2.7$ K) is hardly visible, suggesting that for the ideal 2 DH magnet there is no phase transition in $C_V$.

An interesting experiment on the dependence of $T_N$ on anisotropy for $K_2MnF_4$ ($T_N = 45$ K) has been performed by Breed e. a. [19], who studied the change in $T_N$ upon introducing small amounts of Fe in $K_2FeF_4$ the preferred direction for the sublattice magnetization lies perpendicular to the C-axis (a crystalline field effect) so that the anisotropy in $K_2Mn_{1-x}Fe_xF_4$ may be matched to zero, at least in principle. It has been found, analyzing $\chi$ data, that $T_N$ decreases not more than 20 \% and reaches a minimum of about $37$ K at 2.8 \% Fe. The magnetic behaviour around this concentration becomes rather complicated so that the experiment is not more than an indication that there is a finite $T_N$ also for $H_N/H_E \rightarrow 0$.

More conclusive are the experiments on the ferromagnetic $S = \frac{1}{2}$, $CuCl_2(C_{x}H_{2x+1}NH_3Cl)_2$ series. Figure 5 shows the heat capacity [6] of a typical example. The $C_V$ versus $T$ curve, from which the lattice contribution is not subtracted, shows a small peak at the critical temperature defined as that temperature at which the susceptibility becomes very large [5] and reaches at least in one direction values of the order of that to be expected for a ordinary ferromagnet. The heat capacity a few tenths of a degree above and below this $T_c$ are easily connected by a continuous monotonous curve, which suggests that the phase transition is no essential part of the curve. Moreover, when going through the series of ferromagnetic compounds the energy content of the peak varies drastically between $10^{-4}$ and $10^{-2}$ of the total magnetic energy ($\lambda JS^2$ per atom). This suggests once more that the ideal system would have a continuous $C_V \sim T$ curve and the actual $\lambda$-peak is due to deviations from the ideal system. If we now take the latter statement serious, we can say that we have an experimental measure for these deviations, i. e. the energy content of the $\lambda$-peak in the heat capacity. If this is the case we expect a relation between $kT_c/J$ and $E_{peak}/\lambda JS^2$ such that $kT_c/J$ is the lower the weaker is the anomaly in $C_V$. This relation is shown in figure 6, where data for the...
CuCl$_2$(C$_{2}$H$_{2}$+,NH$_3$Cl)$_2$ and CuBr$_2$(C$_{2}$H$_{2}$+,NH$_3$Br)$_2$ series with $n = 1 \ldots 5$ are included. It is found that for a vanishingly small heat capacity anomaly $kT_C/J$ extrapolates to $T_C/\theta = 0.22$ ($\theta$ is the paramagnetic Curie temperature).

We consider figure 6 and 4 together as a real experimental proof that the quadratic Heisenberg magnet with $S = \frac{1}{2}$ has no phase transition in the heat capacity. Also, figure 6 may be considered as a positive indication for the existence of a critical point in $\chi$ at $T_C > 0$.

Note, however, that the extrapolation in figure 6 involves that for any real system the divergency in $\chi$ is accompanied by a transition to long range-order since, however small is the heat capacity anomaly, it always increases $T_C$ above its ideal value. It is unlikely that arbitrary small but finite anisotropy or interaction in the third dimension result in long range order at $T_C/\theta \geq 0.22$. We suggest that the fact that any real crystal has a finite demagnetizing factor and thus, in combination with a finite anisotropy, a tendency to form Weiss domains, may be responsible for this. If the correlation length becomes larger than the dimension of domains in the long range ordered ferromagnetic state would be, dipolar interactions ranging over macroscopic distances may result in long range order. It should be mentioned that, since for the copper compounds the anisotropy within the a-b plane is much smaller than that in the a-c plane, the critical temperature found in figure 6 may be representative for a model in between Heisenberg and plane rotator (2 dimensional spin) magnet.

III. The interest of non ideal layer type magnets. —

One may ask, in view of the limited information one may get about the SK phase transition, what for instance is the interest of the widely spread investigations on the antiferromagnetic fluorides. Part of the interest lies in the fact that for these layer type antiferromagnets the amount of short range order immediately above $T_N$ is much larger than for 3 dimensional ones: about 90 percent of the magnetic energy is removed above $T_N$ for low $S$ values. This means that for 2 D antiferromagnets the critical temperature region has been largely extended. This is demonstrated in figure 7 where the N. M. R. line width of fluorines in K$_2$MnF$_4$ is plotted versus $T$ [20, 21, 22]. Whereas in 3 D-systems one observes the increase of $\Delta$ only in a narrow range above $T_N$, here $\Delta$ increases gradually for the F$_1$ nuclear having one Mn neighbour, starting at $T = 2 T_N$ already. The experiments give information on the dynamic properties of the spin system, $S(K, \omega)$ and $\chi(K, \omega)$ (where $S(K, \omega)$ is the power spectrum), like that obtained in more detail in neutron diffraction experiments.

The advantage of N. M. R. experiments is their relative cheapness, the disadvantage is that the line width is a weighted average over the fluctuating spectrum as a function of $K$ and at $\omega$ about 0. Within a theoretical model, however, the line width can be calculated and hence the experiments can be used as a test for theoretical descriptions of spin dynamics [23].

![Fig. 7a and 7b. — The N. M. R. line width for fluorine nuclei in K$_2$MnF$_4$ and KMnF$_3$. The line width $\Delta$ increases with decreasing temperature for F$_1$ having only one Mn neighbour. Note the wide temperature range in which the experiment shows the critical slowing down of the Mn exchange fluctuations. The fluorines F$_{II}$ and those in KMnF$_3$ have two Mn neighbours, which become correlated and start cancelling each other. This results in a reduction of the amplitude of the fluctuating field, which dominates the decrease in fluctuating frequencies.](image-url)

An important result from investigations on layer type fluorides is the confirmation of the existence of zero point spin reduction in antiferromagnets. Before 1967 experiments on spin reduction were rather contradictory, essentially related to the fact that for 3 D antiferromagnets the predicted reduction is only small and of the order of a number of (not very well known) corrections. As was emphasized by Lines, layer type antiferromagnets have a 2.5 times larger spin reduction than 3 D ones.

We demonstrate the existence of spin reduction in table I, where experimental data on K$_2$MnF$_4$ and
Rb$_2$MnF$_4$ are compared with those for the corresponding perovskites. Since, as shown in figure 1, the immediate environment and the Mn-F distances are very similar in the two types of compound, the experimental uncertainties when comparing the spin reduction are considerably reduced. In neutron diffraction experiments the difficulty is the Mn form factor, in N. M. R. and nuclear heat capacity experiments it is the value of the h. f. s. constant A. The difference between the 2 D and 3 D compounds, as illustrated in figure 8 for the nuclear heat capacity, places the spin reduction beyond doubt. The differences between the uncorrected values of $<S>$ and $A <S>\text{,}$ respectively, are very near to the values derived within first order spin-wave theory [24] which predicts a reduction of 0.197 and 0.078 for 2 and 3 dimensions, respectively (4.8 \% for Mn).

**Figure 8.** The heat capacity of Rb$_2$MnF$_4$ and RbMnF$_3$ below 1 K plotted as $CT^2$ versus $T^2$. The figure shows the nuclear contribution to be different for the two compounds, in spite of their practically equal A. (Measured by Colpa e. a. [23]).

### Table I

Demonstration of spin reduction in antiferromagnets by comparing two and three dimensional structures

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Compounds</th>
<th>$A &lt;S&gt;$</th>
<th>$A &lt;S&gt;$</th>
<th>diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>or $&lt;S&gt;$</td>
<td>or $&lt;S&gt;$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 D</td>
<td>3 D</td>
<td></td>
</tr>
<tr>
<td>neutr. diff [25]</td>
<td>Rb$_2$MnF$_4$, RbMnF$_3$</td>
<td>4.54 $\mu_B$</td>
<td>4.69 $\mu_B$</td>
<td>3.5</td>
</tr>
<tr>
<td>resonance [26, 27],</td>
<td>K$_2$MnF$_4$, KMnF$_3$</td>
<td>643.5 MHz</td>
<td>676 MHz</td>
<td>5.0</td>
</tr>
<tr>
<td>[26, 28]</td>
<td>Rb$_2$MnF$_4$, RbMnF$_3$</td>
<td>642.4 MHz</td>
<td>687.8 MHz</td>
<td>7.0</td>
</tr>
<tr>
<td>heat cap. [23]</td>
<td>Rb$_2$MnF$_4$, RbMnF$_3$</td>
<td>3.14 x 10$^{-2}$ K</td>
<td>3.30 x 10$^{-2}$ K</td>
<td>5.5</td>
</tr>
</tbody>
</table>

The observed differences have to be corrected for the dipolar field in the layer structure (0.3 \%), the anisotropy (1.1 \%) and for the indirect h. f. s. structure ($\sim 0.6$ \%) [29].

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