Effect of magnetic dilution on the critical temperature of few dimensional antiferromagnetic $CuWO_4$

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The dependence of the magnetic ordering temperature of the $Cu_pZn_{i-p}WO_4$ system on the copper-ion concentration p is investigated. The concentration dependence of the critical temperature is calculated for a two-dimensional model of a magnetic substance with strongly differing exchange interactions between nearest ions distributed in various directions. It is shown that the behavior of a system intermediate between a one-dimensional and two-dimensional system differs essentially, when magnetically diluted, from that of an ideal few-dimensional system.

In the study of phase transitions in concentrated magnets, great interest attaches to an investigation of the possibility of preserving the long-range magnetic order when the magnetic ions are replaced by diamagnetic impurities. The determination of the critical concentration of the magnetic ions p_c, below which establishment of long-range order becomes impossible, and investigations of the dependence of the critical temperature T_c of the mixed system on the concentration, can be used to verify the correctness of the theoretical description of a magnetically-concentrated crystal, particularly the conclusions drawn concerning the values of the exchange interactions and the type of magnetic structure of the crystals.

It should be noted that the problem of phase transitions in magnetically-dilute crystals has been very little studied both theoretically and experimentally, owing to the obvious complexity of the problem. In dilute systems it is impossible to use the modern technique of describing the magnetic-excitation spectrum on the basis of the use of a rigorous periodic magnetic structure, since the distribution of the magnetic ions in the crystal is statistically averaged. Other methods of describing magnetically-dilute systems, which offer a correct qualitative description of their behavior upon dilution, are as a rule very cumbersome. Nonetheless, for magnets with simple structure geometry (such as crystals with high crystal-lattice symmetry, where the exchange interaction of the magnetic ion with all the nearest neighbors can be regarded to be the same), significant results were obtained and were corroborated by experiment. It was shown, in particular, that the critical concentration in the system is determined principally by the dimensionality of the magnetic structure, and is practically independent of the magnitude and anisotropy of the exchange interaction, while the $T_c(p)$ curve decreases linearly with decreasing p at high concentrations and is rapidly cut off towards $T = 0°K$ in the vicinity of p_c. For crystals with low structure symmetry, however, for which the assumption that the energies of the exchange interaction of the ions with the nearest neighbors are equal is incorrect, there is in essence neither theory nor experiment.

Of particular interest in this respect are low-dimensionality magnets, which are characterized by a noticeable difference between the exchange interactions along different directions in the crystal. A typical representative of this kind of system is copper tungstate, which has a rather complicated low-symmetry crystallographic structure. By starting from the results of the x-ray-structure[1] and neutron-diffraction[2] investigations of $CuWO_4$, it can be assumed that the magnetic structure of this crystal has low dimensionality and consists of weakly-interacting chains of copper ions. The magnetic structure of copper tungstate can be regarded as a two-dimensional lattice with exchange interactions J_1 and J_2 in mutually perpendicular directions, which are of opposite sign and differ greatly in magnitude. Within the framework of this model, we have analyzed the magnetic susceptibility[3] and the EPR spectrum[4], and also calculated the Neel temperature of $CuWO_4$[5], which describe well the anomalous behavior of this antiferromagnet.

To study the influence of the magnetic dilution on the magnetic properties of $CuWO_4$, due to its low-dimensional magnetic structure, we have investigated the mixed system $Cu_pZn_{1-p}WO_4$ in a wide range of concentrations p. The diamagnetic analog of $CuWO_4$ was chosen to be zinc tungstate, being the closest to it in the series of tungstates of divalent metals with respect to the crystal-structure parameters and ionic radius of the metal. We have investigated the temperature dependences of the magnetic susceptibility and of the EPR spectrum along the principal magnetic axes of this system of single crystals.

The EPR spectrum was investigated with a 4-mm-band radio spectrometer based on an SP-47 commercial electromagnet in fields up to 33 kOe; this enabled us to trace in detail the broadening of the resonant line as the Neel point was approached. Measurements of the susceptibility were carried out by the Faraday method with the sample placed in a magnetic field with a vertical gradient, using a setup similar to that described in[6]. In both cases the sample was insulated from the cryogenic bath by a composite vacuum-mylar thermal insulation. The thermally insulated volume was filled with the heat-exchange gas (helium) at a pressure of several mm Hg to equalize the temperatures of the sample, the thermometer, and the heater, which were placed inside this volume. A similar system of thermal insulation of the working volume, which makes it possible to cover continuously the temperature ranges between the boiling points of cryogenic liquids, is described in[7].

The temperature was measured with sensitive resistance thermometers (carbon and semiconductor) below 20° K and with a copper-constantan thermocouple above this temperature. In both installations, the error in the sample temperature did not exceed 0.3° K. The Neel temperature was determined from the vanishing of the EPR signal and from the appearance of the characteristic breaks on the plots of the magnetic susceptibility against the temperature.

The dependence of the temperature of the magnetic

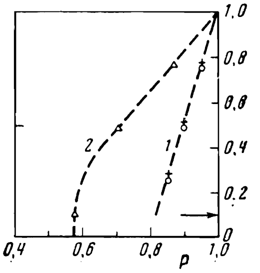

FIG. 1. Concentration dependence of the Neel temperature of $CuPZn_{1-p}WO_4$ single crystals (curve 1). The experimental points were obtained from EPR data (+) and susceptibility data (O). The arrow indicates the minimum temperature reached in the experiment. Curve 2—for $K_2Co_pMg_{1-p}F_4$.

ordering of the $Cu_pZn_{1-p}WO_4$ system on the copper-ion concentration turned out to be quite unusual; it is illustrated in Fig. 1. The figure shows for comparison also the similar dependence for a typical two-dimensional antiferromagnetic $K_2Co_pMg_{1-p}F_4$[8]. As seen from Fig. 1, the critical concentration of the system, which can be obtained by extrapolating the $T_N(p)$ curve to zero temperature, is very high, $p_c \approx 0.8$. This value of p_c is not predicted by the theory developed for magnets with a simple geometry of the structure. p_c ranges from 0.15 to 0.3 for ideal models of three-dimensional magnets, from 0.5 to 0.6 for two-dimensional ones, and $p_c = 1$ for one-dimensional magnets. Real intermediate models have hardly been considered in the theory, yet, as will be shown below, allowance for weak interchain exchange in the case of the one-dimensional magnet (or interlayer exchange in the two-dimensional case) is important in principle.

The presence of weak interactions between chains (or between layers) causes the character of the concentration dependences of the ordering temperature of the magnets to differ greatly, in the case of magnetic dilution, from the analogous relations that take place in ideal one-dimensional or two-dimensional magnetic structures. Allowance for the peculiarities of the two-dimensional magnetic structure of copper tungstate, where the exchange interactions in a plane differ greatly for two mutually perpendicular directions, can explain the anomalous behavior of the phase-transition temperature of this antiferromagnet in magnetic dilution.

The calculation of the concentration dependence of the critical temperature of a two-dimensional system and the determination of the critical concentration were carried out by us by a method (which seems to be the most promising for the determination of the characteristics of magnetically-dilute systems) based on expanding the susceptibility of the mixed system in powers of the concentration, followed by a determination of the necessary concentration as the limit of the convergence of the series at a given temperature. A number of workers[9-11] have used this method successfully to analyze the behavior of two-dimensional and three-dimensional magnets with simple magnetic-dilution structure geometry. For a ferromagnet, the magnetic susceptibility of the mixed system can be represented in the form of a sum of susceptibilities of isolated clusters

$$\chi(T)=\sum_{n\alpha}N_{n\alpha}\chi_{n\alpha}(T), \qquad (1)$$

where $N_{n\alpha}$ is the number of clusters of type α, each cluster consisting of n particles. In the general case, for a lattice containing N points, which can be occupied when the lattice is randomly filled, we have

$$N_{n\alpha}=NA_{n\alpha}p^n(1-p)^m. \qquad (2)$$

Here $A_{n\alpha}$ is the number of possible realizations of the cluster in the lattice, m is the number of places for the nearest neighbors of the cluster, which should be empty if the cluster is assumed isolated. Then the susceptibility can be expressed in the form of a series in powers of the concentration (the notation is standard):

$$\chi(T)=\frac{Ng^2\beta^2}{kT}p\sum_{n=0}^{\infty}a_n(T)p^n \qquad (3)$$

and, calculating the first few terms of the series, they can be used to estimate its convergence radius. Thus, p is the concentration that must be obtained in the system in order for the susceptibility to become finite at $T_c(p)$.

In this analysis, the critical concentration is that at which the ordering temperature is minimal, i.e., $T_{c,\min}(p_c) = 0$. As shown in[12], the critical concentration for a ferromagnet does not depend on the model of the interaction (Ising or Heisenberg), and is a topological property of the lattice, so that in final analysis it is determined by the average size of the clusters, which reach infinitely large dimensions as p_c is approached.

In turn, the question of the average cluster dimensions for a random distribution of the particles in the lattice was extensively investigated in the so-called "filtering problem," where the value of p_c was calculated with high accuracy with a computer by the Monte Carlo method for different types of crystal lattices[13]. The results of the calculations of p_c by the last method can be used to verify the predictions of the method of expanding the susceptibility, since they yield the minimum possible concentration of the impurity ions necessary to realize a cluster of infinitely large dimension. In the high-temperature region, the criterion for the validity of the described method can be the method of high-temperature expansion (the value of the ratio $kT_c(1)/J$ for different interaction models). Thus, in the analysis of the corresponding types of clusters realized in a concrete lattice, it is possible to take into account by the method chosen by us the presence of two different exchange interactions between the nearest neighbors, since these interactions determine the susceptibility of the considered clusters.

Knowing several terms of the series (3), we can seek its convergence radius, in order to determine the concentration p at a given value of $T_c(p)$, in the form $\lim |a_n|^{-1/n}$ or $\lim |a_n/a_{n+1}|$ as $n \to \infty$. At the same time, calculation of the coefficients a_n for large values of n becomes difficult, particularly in the Heisenberg model, since it requires calculation of the eigenvalues of a matrix of order 2^n in order to obtain the susceptibility of a cluster consisting of n particles. Elliott and Heap[9,10], analyzing in a similar manner the $T_c(p)$ dependence for different lattice types, conclude that if the number of the power-series terms is limited, a sufficiently good approximation in the Ising model for plane and three-dimensional lattices is obtained by linearly extrapolating to $1/n \to 0$ the values of $a_2(T)$ and $a_4(T)$, or $a_2(T)$ and $a_3(T)$, or $a_3(T)$ and $a_4(T)$ in the entire temperature interval. In addition, the $T_c(p)$ dependence can be qualitatively determined for the Ising model from the value of the coefficient $a_3(T)$, although the concentrations in this case, including p_c, are underestimated.

In the case of the Heisenberg model, the initial coefficients $a_n(T)$ do not behave monotonically in the low-temperature region, this being due to the peculiarity of the arrangement of the low-lying levels in the energy spectrum of this model, since these levels form an almost continuous band in the case of a large cluster and enter with a large statistical weight in its magnetic susceptibility. This makes it necessary to consider terms of higher order, and consequently clusters with larger dimensions. At the same time, the purely topological properties of the magnetic lattice, including different exchange interactions between nearest neighbors, can be demonstrated by using the Ising model, for in this case the cluster analysis is much simpler. In addition, for a dilute Ising magnet one obtains sufficiently reliable results at a limited number of terms of the series (3).

We calculated the magnetic susceptibilities of clusters with $n \leq 4$ realized in the case of planar quadratic lattice with two different exchange interactions between nearest neighbors, under the assumption that the occupation of the lattice points is statistically independent. We considered an Ising model with particle spin $S = 1/2$. For the ferromagnetic clusters ($J > 0$) we calculated the magnetic susceptibility with the aid of a Hamiltonian in the form

$$\mathscr{H}=-2J_{ik}\sum_{i\neq k}S_i^zS_k^z-g\beta H\sum_i S_i^z, \tag{4}$$

which takes into account the exchange interaction in the external magnetic field H applied along the z axis.

We note incidentally that in the case of an antiferromagnetic system ($J < 0$) the usual magnetic susceptibility has no singularity at the phase-transition point[14]. Therefore, when antiferromagnetic clusters or mixed-type clusters are considered, it is necessary to determine the so-called staggered susceptibility, by introducing into the Hamiltonian a change in the direction of the external field over the lattice sites in accordance with the expected magnetic structure, which appears when the system goes over into the ordered state[9,11]. In this case the Hamiltonian takes the form

$$\mathscr{H}=2|J_{ik}|\sum_{i\neq k}S_i^zS_k^z-g\beta H\left(\sum_i S_i^z-\sum_k S_k^z\right), \tag{5}$$

where the subscripts i and k pertain to ions from different sublattices. Calculations of the ordinary and staggered susceptibility using (5) and (6) lead to the same result in the Ising model, so that the influence, considered by us, of the difference between the exchange interaction J_1 and J_2 on the form of the concentration dependence of the ordering point will not depend on the sign of the exchange interaction.

As already mentioned, a qualitatively correct description of the concentration dependence of the critical point $T_c(p)$ of an Ising magnet can be obtained by analyzing the temperature dependence of the coefficient $a_3(T)$ of the series (3), bearing in mind that the values of the concentrations corresponding to the considered temperatures are underestimated. The sought values of the concentration are given here by $p = [a_3(T)]^{-1/3}$.

As calculated with the aid of the M-222 computer for different ratios $\gamma = J_1/J_2$ in our model, they are shown in Fig. 2. As seen from the figure, the difference between the exchange integrals does not affect the critical concentration p_c, the value of which turned out to be 0.347, since the susceptibilities of clusters of all types in the ground state do not depend on J as $T \to 0$. However, the course of the $T_c(p)$ changes significantly with changing γ. At $\gamma = 1$, the value of $T_c(p)$ is proportional in practice to p at large concentrations, and the $T_c(p)$ curve drops rapidly as p_c is approached, and coincides with the curve obtained by Elliott and Heap for a planar quadratic Ising magnet.

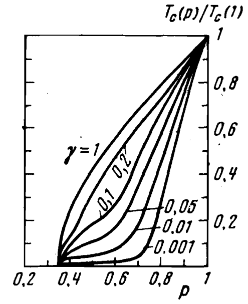

FIG. 2. Concentration dependence of the critical temperature, calculated for a two-dimensional model at different ratios of the exchange integrals $\gamma = J_1/J_2$.

At small γ, corresponding to a large difference between the exchange integrals J_1 and J_2, the $T_c(p)$ curve drops steeply with decreasing p in the region of large concentrations, and has a gently-sloping dependence on p with further decrease of the concentration. The gently-sloping section of the $T_c(p)$ curve corresponds to the low-temperature region. Taking into account the remarks made above concerning the effect of the limited number of terms in the series, it is obvious that to obtain the true dependence of the critical temperature on the concentration as the limit of the convergence of the series it is necessary to shift the $T_c(p)$ curves into the region of higher concentrations. Thus, when the value $a_4(0)$ is used, we obtain $p_{c(4)} = 0.373$, and by linearly extrapolating the values of $p_{c(3)}$ and $p_{c(4)}$ to $1/n \to 0$, we can obtain $p_c = 0.5$. However, in the calculations of the coefficient $a_4(T)$ at $T > 0$, aimed at a similar extrapolation in the entire temperature interval, it is necessary to consider clusters made up of groups of five interacting spins, of which 21 types are realized in the lattice considered by us. Owing to the obvious complexity of the calculations, we have limited the analysis of the series (3) to the coefficient $a_3(T)$.

At the same time, the calculation results already offer a qualitative explanation of the anomalous dependence of the Neel temperature on the concentration of the magnetic ions, observed for the $Cu_pZn_{1-p}WO_4$ system, if account is taken of the considerable difference between the exchange interaction energy in $CuWO_4$. The abrupt decrease of the critical temperature of the system with increasing magnetic dilution can be treated as a section of the $T_c(p)$ curve in the region of high concentrations. The gently-sloping section of the curve for the region of lower concentrations can apparently be reconstructed by performing the measurement at lower temperatures than reached in our experiments, inasmuch as at $T \approx 2°K$ the samples containing 80% and less copper ions still remain paramagnetic.

The $CuWO_4$ structure occupies an intermediate position between the one-dimensional and two-dimensional magnetic structures, and this is precisely the cause of the appearance of a low-temperature gently-sloping section of the $T_c(p)$ curve, inasmuch as for an ideal one-dimensional structure the critical concentration should be equal to unity according to the analysis described above. It appears that a similar situation in the low-temperature region should be observed also for systems close to ideal two-dimensional structures, for example $K_2Mn_pMg_{1-p}F_4$ and $K_2Co_pMg_{1-p}F_4$[8], if one introduces into consideration a small exchange between layers, which really exists in these crystals. This will make it necessary to take clusters of the "three-dimensional" type into account, and the true value of the critical concentration should shift in this case to the value $p_c \approx 0.2-0.3$, as for usual three-dimensional structures. The region where the $T_c(p)$ has a sharp inflection will then be located near $p \approx 0.5-0.6$, and can be connected with the experimentally observed critical concentration.

One should obviously expect also the appearance of anomalies in the concentration dependence of the ordering temperature of a three-dimensional magnet in the region of small concentrations (smaller than 0.15—0.3), if account is taken of the existence of interactions of the magnetic ion not only with the nearest neighbors, but also with the more remote ones. Therefore the concept of "critical" concentration is apparently arbitrary and can be applied to ideal models.

The study of phase transitions in magnetically-dilute systems at concentrations when weak long-range forces are significant is of interest both theoretically and experimentally. However, for investigations at low concentrations, in order to determine the true form of the $T_c(p)$ curve, it is necessary to use extremely low temperatures.

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