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Dependence of the magnetic ordering temperature on dilution in a 3D XY insulating ferromagnet

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Abstract

Ferromagnetic polycrystalline $\text{Fe}[\text{Se}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$ is examined, as are several dilute versions of it containing diamagnetic $\text{Zn}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$, present to the extents 3.6, 7.9, 13.7 and 20.2%. The magnetic ordering temperature decreases much less rapidly with dilution than predicted by any standard model such as the nearest neighbor 3D Ising, XY and Heisenberg ones, and the initial slope $-(dT_c/dx)/T_c$ is well below unity. A curvature change of $T_c(x)$ appears at approximately 14% dilution. Extensions of simple models do not account for the results. It is possible, perhaps, that molecular shape factors lead to effectively nonrandom dilution, unexpectedly surviving ferromagnetic interactions, and thus to the unprecedented $T_c(x)$.

1. Introduction

Among insulating materials the pentacoordinate iron(III) molecular ferromagnet, $\text{Fe}[\text{Se}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$, hereafter $\text{Fe}[\text{DSC}]_2\text{Cl}$, is perhaps the only one known to exhibit three-dimensional (3D) XY model behavior [1]. Exchange interactions occur via intermolecular $\text{Se}\dots\text{Se}$ contacts, the selenium atoms being covalently bonded to the iron, leading to ferromagnetic ordering near 3.4 K. The unusual site symmetry at the iron permits an intermediate spin, $S = 3/2$, crystal field electronic ground term to result. Spin–spin and spin–orbit interactions are reflected in spin Hamiltonian terms expressing axial and rhombic crystal field distortions of the form $D[\hat{S}_z^2 - S(S+1)/3]$ and $E[\hat{S}_x^2 - \hat{S}_y^2]$, respectively. Analysis of single crystal susceptibility data yielded $D/k = 6.9_5$ K and $E/k = -0.1_4$ K, with a corresponding zero-field splitting between ground $|\pm 1/2\rangle$ and excited $|\pm 3/2\rangle$ Kramers doublets of 13.9 K. At temperatures well below the magnitude of the zero-field splitting population of the ground doublet predominates, and the system acquires XY character because of the anisotropic g'_i ($i = x, y, z$) values on an $S' = 1/2$ basis [1].

A contrasting situation in a closely related material is that of $\text{Fe}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$, hereafter $\text{Fe}[\text{DTC}]_2\text{Cl}$, where a ferromagnetic transition occurs near 2.5 K [2]. (DTC stands for the dithiocarbamate ligand, as DSC above stood for the diselenocarbamate ligand.) Both the molecular and the crystal

structures of the two systems are the same, the unit cell of the selenium material being 5.2% larger because of the greater size of Se versus S. In $\text{Fe}[\text{DTC}]_2\text{Cl}$, however, the D parameter is negative and the consequent zero-filled splitting is 7.0 K. In this case the ground Kramers doublet is $|\pm 3/2\rangle$, with $|\pm 1/2\rangle$ the excited doublet. The g'_i values of the ground doublet on an $S' = 1/2$ basis have anisotropic character of Ising type rather than XY . (The critical behavior of $\text{Fe}[\text{DTC}]_2\text{Cl}$ has been studied extensively and conforms more nearly to chiral model behavior than to that of any standard universality class [3], though the more general magnetic properties are somewhat Ising-like.)

The dilution dependence of T_c in $\text{Fe}[\text{DTC}]_2\text{Cl}$ has been studied, though over only a limited composition range up to 4.0% diamagnetic admixture [2]. The detailed dependence of T_c on x (diluent) was not as the somewhat limited theoretical calculations might lead one to expect. It should therefore be interesting to perform a similar study on a very closely related ferromagnetic system but one of contrasting spin anisotropy. That is the purpose of the present work.

2. Experimental details

$\text{Fe}[\text{DSC}]_2\text{Cl}$ was prepared as described previously [1]. A necessary but uncommon starting reagent, CSe_2 , was purchased on special order from ICN Biomedicals, Inc. The diamagnetic diluent, $\text{Zn}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$, hereafter $\text{Zn}[\text{DTC}]_2$,

is readily prepared by reaction of zinc acetate with sodium diethyldithiocarbamate in absolute ethanol solution, the desired product precipitating out. Magnetic $\text{Fe}[\text{DSC}]_2\text{Cl}$ and nonmagnetic $\text{Zn}[\text{DTC}]_2$ were dissolved in methylene chloride to form a series of solutions of various nominal relative compositions. Slow evaporation of the solvent, at ca 5°C and in the dark to inhibit degradation of slightly light sensitive $\text{Fe}[\text{DSC}]_2\text{Cl}$, occurred over about a week. The polycrystalline material obtained was dried overnight under vacuum and used for magnetic measurements. No single crystals of even modest mm^3 dimensions, which might serve for low field vibrating sample magnetometer (VSM) measurements given instrumental sensitivity and a large ferromagnetic signal, were available, and hence the use of polycrystalline samples. Visual examination of the polycrystalline materials under a microscope revealed no signs of segregation into purple-blackish $\text{Fe}[\text{DSC}]_2\text{Cl}$ and whitish $\text{Zn}[\text{DTC}]_2$. Experience with various mixed magnets [4] suggests that even unit cell volume differences per formula unit as large as 11.7% do not necessarily prevent one component from dissolving uniformly in another. The unit cell volume per molecule is about 11.3% smaller in $\text{Zn}[\text{DTC}]_2$ than in $\text{Fe}[\text{DSC}]_2\text{Cl}$. So while substantial, the difference is not prohibitive. One might even anticipate that the zinc molecule would have less trouble substituting in the iron compound lattice given its smaller size. Following magnetic measurements the actual samples employed were subjected to elemental analysis for iron and zinc by atomic absorption spectrophotometry, leading to dilution levels of 3.6%, 7.9%, 13.7% and 20.2% Zn component. Uncertainties in these values are at the 0.1–0.2% level.

In the previous dilution study of $\text{Fe}[\text{DTC}]_2\text{Cl}$ the slightly more obvious diamagnetic diluent $\text{As}[\text{DTC}]_2\text{Cl}$ was employed [2]. That substance was found not to work here because of an unwanted reaction between it and the Se-containing iron component on dissolving the two in methylene chloride for obtaining mixed solid material. No such phenomenon occurred on employing the zinc diluent. In either case it was not considered necessary to attempt a difficult and expensive (CSe_2) synthesis of diluent molecules containing Se rather than S, i.e., DSC rather than DTC forms, since the point was only to obtain a species of roughly comparable size that could substitute in the host $\text{Fe}[\text{DSC}]_2\text{Cl}$ lattice and which would be diamagnetic. In the present work substantially larger diluent levels were attainable than in the case of $\text{As}[\text{DTC}]_2\text{Cl}$ in $\text{Fe}[\text{DTC}]_2\text{Cl}$ previously. This is presumably a consequence of the slightly larger unit cell size of $\text{Fe}[\text{DSC}]_2\text{Cl}$ relative to $\text{Fe}[\text{DTC}]_2\text{Cl}$, and the somewhat smaller size of $\text{Zn}[\text{DTC}]_2$ relative to $\text{As}[\text{DTC}]_2\text{Cl}$.

Magnetization and susceptibility (M/H) measurements were made using a vibrating sample magnetometer system. Data shown in the following are corrected for demagnetization and are considered accurate to $\pm 1.5\%$, with a precision much better than this. Samples were packed polycrystalline aggregates, of variable mass from 25 to 150 mg, measured to ± 0.01 mg. Temperatures were measured with a calibrated resistance thermometer located in immediate proximity to the sample, and are estimated to be accurate to ± 0.005 K with

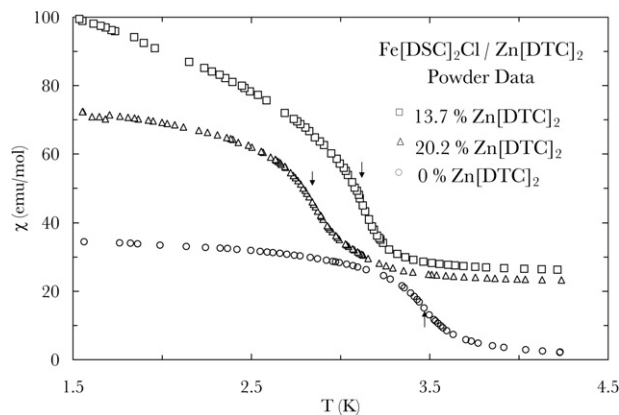


Figure 1. Molar magnetic susceptibility versus temperature in moderately low applied fields for polycrystalline $\text{Fe}[\text{DSC}]_2\text{Cl}$ and two dilute compositions of the same. Data for 13.7% and 20.2% $\text{Zn}[\text{DTC}]_2$ diluted material are shifted up for clarity. Arrows indicate location of the inflection point in susceptibility, which is identified with T_c .

substantially better precision in the helium T -range. For low field measurements an external power supply was used to cancel most of the residual field of the 12" electromagnet. Magnetic field values are accurate to $\pm \max(2 \text{ G}, 0.1\%)$, again with much better precision.

3. Measurements and analysis

Previous work on $\text{Fe}[\text{DTC}]_2\text{Cl}$ and $\text{Fe}[\text{DSC}]_2\text{Cl}$ has shown that T_c can be fairly accurately estimated from the point of inflection (as the ferromagnetic susceptibility increases with decreasing temperature) in $\chi(T)$ of a polycrystalline sample in relatively low applied fields. Values thus estimated are found to be within 0.01–0.02 K of T_c values more systematically determined, e.g., from critical law fits to single crystal easy axis data, or Arrott plot analysis of magnetization data along the easy axis [1, 2]. This choice (inflection), a change in sign in the second derivative of a thermodynamic quantity like the susceptibility, may also be rationalized as appropriate for signaling a continuous (magnetic) phase transition. The precision of the individual T_c estimates from inflection point locations is about 0.01–0.02 K depending on the particular data set examined.

Shown in figures 1 and 2 are the moderately low field susceptibilities of the four dilute compositions prepared and that of pure $\text{Fe}[\text{DSC}]_2\text{Cl}$. The applied fields were between 90 and 101 G for four of the sets shown, 207 G for 13.7% $\text{Zn}[\text{DTC}]_2$. In each case the applied field was measured and recorded continually to the nearest 0.1 G as data were collected, and remained constant to within 1% over the measurements. With fields of the size indicated fairly smooth looking plots of $\chi(T)$ are obtained. These plots show only one inflection point, arguing against the possibility that different portions of the measured sample represent material of significantly different composition. It is important to note also that in every case analogous data were collected using a substantially smaller field, which over the five compositions

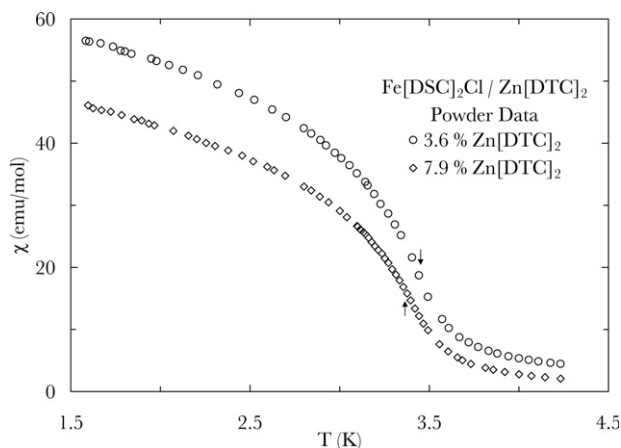


Figure 2. Molar magnetic susceptibility versus temperature in moderately low applied fields for two other dilute compositions of Fe[DSC]₂Cl in polycrystalline form. Data for 3.6% Zn[DTC]₂ are shifted up for clarity. Arrows indicate the inflection point estimate for T_c .

shown spanned the range 17.55–21.50 G and which was measured to the nearest 0.05 G continually, remaining constant to within 2% or better over the measurements. Because of the several times smaller field used and the precision of the magnetometer readout, the resulting susceptibility data produce a somewhat noisier $\chi(T)$ plot. Because of this, the inflection point is in some cases slightly less clear, but for every one of the five compositions the location of this inflection was the same (mostly) or within 0.03 K of the value estimated from the smoother higher field data. Nor were any systematics in the deviation observed, i.e., T (inflection) might be slightly larger or slightly smaller in the larger versus the smaller field case. It is concluded that for the moderate fields employed there is no field dependence to T_c values estimated from inflections in $\chi(T)$, and these can be considered accurate to approximately 0.02 K.

Another method of estimating T_c is by Arrott plot analysis of a series of magnetization isotherms, employing small to moderate field data. For a highly anisotropic ferromagnet like Fe[DTC]₂Cl or Fe[DSC]₂Cl the data should be obtained with the field along the ferromagnetic easy axis. Nevertheless, the approach was tried for the present polycrystalline samples. Rather as in our much earlier study of mixed ferromagnetic Fe[DSC]₂Cl/Fe[DTC]₂Cl [5], it was found that the Arrott method tends to yield a lower T_c than that obtained from the susceptibility inflection point. This can be understood as arising from indirect effects of magnetic anisotropy expressed in the polycrystalline data. The Arrott derived values also vary less regularly with composition than do the inflection derived values. However, Arrott derived ordering temperatures also decrease much more slowly with x near the infinitely dilute limit than do standard theoretical models. Further, the Arrott derived results are slightly more consistent with a $T_c(x)$ form displaying a curvature change than with uniform concave downward curvature.

In figure 3 appear the more reliable inflection derived T_c values versus composition, along with a plausible curve

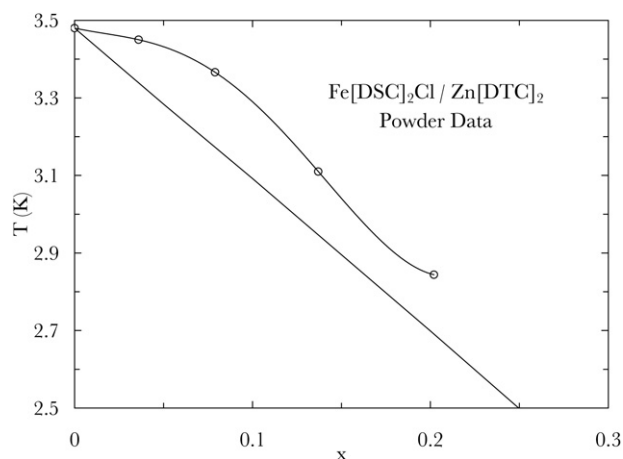


Figure 3. Magnetic ordering temperature versus mole fraction diluent for Fe[DSC]₂Cl diluted with Zn[DTC]₂. Curve through results (open symbols, from susceptibility inflections) is a guide to the eye. For comparison purposes the theoretical dilution dependence for a three-dimensional Ising model, faster falling line, also appears.

through the results. A curvature change appears near $x = 0.14$. The essential shape of this curve is not changed by invoking the previously given uncertainties in T_c and x . While the curvature change depends on the location of one datum (attempts to obtain higher- x material did not succeed), it is believed that the conclusion is reliable given the cited uncertainties.

4. Discussion

For comparison purposes there also appears in figure 3 the essentially common result of various theoretical calculations (0.1% agreement generally) for the simple cubic (3D) Ising model [6]. In the concentration range shown the theoretical dependence is virtually linear and almost the same as mean-field theory gives. For either the Heisenberg or XY sc models $T_c(x)$ drops somewhat more rapidly than for the Ising case. Values for the initial slope, $-(dT_c/dx)/T_c$, have been obtained via effective field theory and given as 1.183, 1.201 and 1.222 for the sc Ising, XY and Heisenberg models, respectively [7]. A separate calculation for the sc XY case gives 1.22 for the initial slope [8]. For more highly coordinated lattices than sc (i.e., bcc and fcc) initial slope values decrease by several per cent with each upward shift in coordination number [7]. A more accurate value for the sc Ising case is also available, 1.06 [9]. For two-dimensional models the initial slopes are definitely larger, by about 20–50% depending on lattice type and spin anisotropy case [7].

The experimental $T_c(x)$ reported here differs significantly from any theoretical prediction. Most striking perhaps is the very small decrease in the transition temperature over the experimental dilution range nearest zero. With a most dilute composition 3.6% Zn[DTC]₂, this is presumably not small enough to yield the infinitely dilute limit, though plausibly close to it. The observed curvature of $T_c(x)$, slightly concave downward, is such that $-(dT_c/dx)/T_c$ in the infinitely dilute limit would be less than an estimate based on the T_c values for $x = 0$ and 0.036. Over this interval $-(\Delta T_c/\Delta x)/T_c =$

0.24 ± -0.02 . This value is much smaller than any theoretical value. While the rate at which T_c falls is significantly larger somewhat beyond $x = 0.036$, the $T_c(x)$ curve remains well above the theoretical dependence for the 3D-Ising model and even more above the 3D-XY and 3D-Heisenberg cases.

In the only other study of a dilute 3D-XY system known to us, antiferromagnetic $[\text{Co}_x\text{Zn}_{1-x}(\text{C}_5\text{H}_5\text{NO})_6](\text{NO}_3)_2$ [10], the composition dependence of the ordering temperature followed only plausibly well the prediction for the sc XY model, the actual results somewhat straddling the theoretical curves for the various sc models (Ising, XY, Heisenberg). The exchange interaction pathways in this system are more regular than those for the material studied in this paper.

The inflection in $T_c(x)$ near $x = 0.14$ has no counterpart in the theoretical dependences already referred to, certainly not at such a modest x (diluent) value and far from any percolation limit. But the standard theoretical treatments assume only near neighbor interactions. Modifications to various predictions concerning the detailed form of dilution dependence, initial slopes, etc. do emerge on incorporating next nearest neighbor interactions as well [11]. There is, for example, a reduction in the initial slopes, though not to values below unity. For the 2D-Ising lattices inflection points can appear in $T_c(x)$, though apparently only for x (diluent) 0.20 or higher [11, 12]. For 3D-Ising lattices changes in the curvature of $T_c(x)$ can also occur, though at rather larger values of x (diluent) than in the 2D case [11]. It should be emphasized that among the not very large number of real systems for which the dilution dependence of T_c has been examined, the data usually do not conform closely to theoretical curves, even those from treatments involving more than nearest neighbor only interactions. Examples include $\text{Ni}_{1-x}\text{Mg}_x(\text{OH})_2$ among 2D systems [13], and $\text{Mn}_{1-x}\text{Mg}_x\text{S}$ among 3D systems [14]. In each of these examples inflections appear in $T_c(x)$, but at dilution levels larger than in the present work. However, the most general result from incorporating next nearest neighbor interactions, that the ferromagnetic state is stabilized if the additional interactions are also ferromagnetic, is consistent with our observation of a $T_c(x)$ higher than the simplest theoretical curves.

Another modification of the simplest theoretical models of dilution introduces correlations governing how the coupling between nearest neighbor magnetic sites depends on the occupancy of neighboring sites by magnetic ions. It is found that the initial slope increases with increasing correlation [15, 16]. Also, the curvature of $T_c(x)$ is such that the rate of decrease in T_c with increasing dilution becomes smaller as the dilution concentration increases; i.e., the curvature is opposite in sign to that exhibited by the experimental results in figure 3 for the lowest dilutions [16, 17]. It is thus qualitatively similar to the dilution dependence seen by us previously for $\text{Fe}[\text{DTC}]_2\text{Cl}$ [2]. It was already pointed out for that dilute system, however, that the detailed observations were not accounted for quantitatively by correlated dilution models. It may be mentioned that in this earlier studied system the initial slope was 1.15 ± 0.11 (over the small dilution interval x (diluent) = 0–0.0039), much larger than for the system examined here.

Superexchange pathways in both $\text{Fe}[\text{DTC}]_2\text{Cl}$ and isostructural $\text{Fe}[\text{DSC}]_2\text{Cl}$ occur via $\text{Fe}-\text{S}(\text{Se})\dots(\text{Se})\text{S}-\text{Fe}$ intermolecular contacts. The relevant $\text{S}\dots\text{S}$ or $\text{Se}\dots\text{Se}$ separations are within a few percent of twice the van der Waals radii of these atoms, so that overlap of wavefunctions is significant. The distinct nonlinearity of the several differently directed intermolecular pathways of the above general type [1, 18] promotes a ferromagnetic (as opposed to antiferromagnetic) exchange interaction. Detailed consideration of the structure and the relevant separations suggests that any given molecule probably interacts with five and possibly six neighbor molecules for which the characteristic $\text{Se}\dots\text{Se}$ separations span a range 3.67–4.08 Å, with two of the smallest type, three intermediate at approximately 3.90 Å, and one of the longest type. It is very difficult to estimate whether molecular shape factors influencing how the diamagnetic diluent molecule goes into the host lattice could lead to a preferential preservation of certain $\text{Fe}-\text{Se}\dots\text{Se}-\text{Fe}$ pathways as opposed to others, though it is perhaps possible. In such case one would have other than completely random dilution, which might provide the beginning of a rationalization of the unusual observed $T_c(x)$. However, it is not believed that substitution of S for Se introduces a significant additional element of randomness. The S occurs only in the diamagnetic $\text{Zn}[\text{DTC}]_2$ molecule, and any prospective $\text{Fe}-\text{Se}\dots\text{S}-\text{Zn}$ intermolecular pathway is not a meaningful exchange connection since the zinc ion is diamagnetic. One would certainly anticipate that a very long superexchange pathway of the type $\text{Fe}-\text{Se}\dots\text{S}-\text{S}\dots\text{Se}-\text{Fe}$, that is involving two sulfur atoms of a $\text{Zn}[\text{DTC}]_2$ molecule, could not be effective. If such an interaction were nontrivial, however, and ferromagnetic, this would offer a potential rationalization of the weak decline in T_c with dilution.

One additional comparison, a somewhat unexpected one perhaps, is worth attention. In the earlier study of mixed ferromagnetic $\text{Fe}[\text{DSC}]_2\text{Cl}/\text{Fe}[\text{DTC}]_2\text{Cl}$ already noted [5], there was found a composition dependence of the ordering temperature reminiscent of what has emerged here. That is, for $\text{Fe}[\text{DSC}]_2\text{Cl}$ rich mixtures, the curvature of the T versus x plot is similar to that in figure 3. Quantitative details are different of course. An inflection in $T_c(x)$, where x is now the mole fraction of the other ferromagnetic component $\text{Fe}[\text{DTC}]_2\text{Cl}$, occurs near $x = 0.40$ rather than 0.14. And the decrease in T_c with admixture of $\text{Fe}[\text{DTC}]_2\text{Cl}$ into majority $\text{Fe}[\text{DSC}]_2\text{Cl}$ is much slower than in the present genuinely dilute system. Thus at $x = 0.20$, that is 20% $\text{Fe}[\text{DTC}]_2\text{Cl}$ content, T_c has fallen by only about 5.3%, whereas it has fallen over 18% for the same x (diamagnetic) here. However, that the shape of $T_c(x)$ is similar in the former all ferromagnetic system does suggest that in the present dilute system it is indeed the survival of more numerous ferromagnetic interactions than anticipated which leads to the unexpected form of $T_c(x)$. So far as we know no similar curve, neither quantitatively nor qualitatively, has been seen in any other dilute material.

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