

Magnetic behavior and magnetic phase diagram of the insulating mixed ferromagnet $\text{Fe}[\text{S}_{2x}\text{Se}_{2(1-x)}\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$

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The title system is a mixture of two isomorphous three-dimensional (3D) ferromagnets. One component, the sulfur system or dithiocarbamate, is approximately describable as a 3D Ising ferromagnet, ordering at 2.458 K. The other component, the selenium system or diselenocarbamate, is approximately describable as a 3D *XY* ferromagnet ordering at 3.463 K. Susceptibilities of polycrystalline samples of the mixed system are Curie-Weiss-like above 20 K. The Weiss constant θ exhibits a pronounced wavelike composition dependence, though always remaining positive. Each mixture is observed to order ferromagnetically. The composition dependence of the ordering temperature, deduced from low-field susceptibility and magnetization measurements, is *S*-shaped, with a somewhat stronger composition dependence on the Se-rich side of the diagram. This form of $T_c(x)$, which seems to be realized for the first time in this mixed system, corresponds to one of the phase-diagram types predicted in earlier theoretical work of Thorpe and McGurn.

I. INTRODUCTION

The behavior of randomly mixed magnetic systems is a topic which has received a great deal of study in the past decade, both theoretical and experimental. Two kinds of systems have received the most attention: (a) those in which competing orthogonal spin anisotropies occur,¹⁻³ the easy axes of magnetic ordering of the pure isomorphous components being perpendicular, and (b) those in which strongly competing ferromagnetic and antiferromagnetic interactions occur,⁴ with consequent frustration. Systems of type (a) can exhibit (apparent) tetracritical points, where four lines of transitions meet, and regions in the *T* composition phase diagram with ordering character intermediate between those of the pure components. A particularly well studied example is $\text{Fe}_{1-x}\text{Co}_x\text{Cl}_2$.⁵⁻⁷ Systems of type (b) can exhibit spin-glass phases, with reentrant behavior occurring in some circumstances. Well studied examples are $\text{Eu}_x\text{Sr}_{1-x}\text{S}$,⁸ and $\text{Rb}_2\text{Mn}_{1-x}\text{Cr}_x\text{Cl}_4$.⁹ Also studied in some detail recently is $\text{Co}_{1-x}\text{Mn}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$.¹⁰ It is also possible to envisage a mixed magnet possessing both competing orthogonal spin anisotropies and competing ferromagnetic and antiferromagnetic interactions; indeed, at least one such example, $\text{Fe}_{1-x}\text{Mn}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, has been examined.¹¹ Another recent example, which appears to exhibit a tetracritical point even though spin anisotropies are not orthogonal, is $[(\text{CH}_3)_3\text{NH}]\text{Co}_{1-x}\text{Ni}_x\text{Cl}_3 \cdot 2\text{H}_2\text{O}$.¹²

However, even in the absence of the special kinds of competition mentioned above mixed magnetic systems remain well worth studying. For example, theoretical predictions¹³ for possible phase boundary shapes have certainly not been exhaustively realized in real systems, and the effects of subtler competitions than those indicated above are far from completely surveyed. With these and other considerations in mind we have prepared and studied a mixed magnetic system,

$\text{Fe}[\text{S}_{2x}\text{Se}_{2(1-x)}\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$, composed of two isomorphous three-dimensional ferromagnets. The molecular structure(s) of the constituents are shown in Fig. 1. In each system the dominant exchange interaction is believed to occur via sulfur-sulfur, or selenium-selenium, overlaps between atoms on different molecules.¹⁴ One component, $\text{Fe}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$, orders at 2.458 K and can be described as approximately Ising-like in its anisotropy; $D/k = -3.32(5)$ K in the principal anisotropy term $D[\hat{S}_z^2 - S(S+1)/3]$, the negative value of *D* making the Ising-like $|\pm \frac{3}{2}\rangle$ doublet low-lying.¹⁵ (Details of the critical behavior¹⁶ differ somewhat from those of the three-dimensional Ising model, and the system may instead fall into a different, recently discovered universality class, feasible for an Ising system which exhibits, symmetry permitting, canted sublattices.¹⁷) The other component, $\text{Fe}[\text{Se}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$, orders at 3.463 K and can be described as approximately *XY*-like in its anisotropy; $D/k = 6.95(10)$ K in a similar anisotropy term, the positive value of *D* making the *XY*-like $|\pm \frac{1}{2}\rangle$ doublet low-lying.¹⁸ Thus competing Ising and *XY* anisotropies

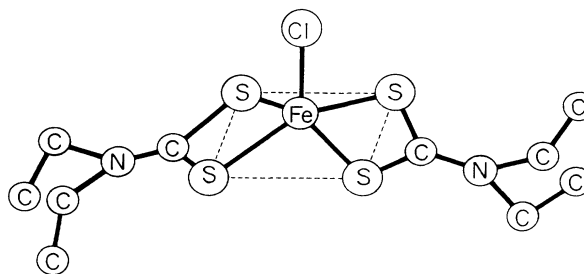


FIG. 1. Molecular structure of $\text{Fe}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$, or of $\text{Fe}[\text{Se}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$ on replacing sulfur atoms by selenium atoms. Hydrogen atoms are not shown.

should occur in the mixture. However, the preferred direction of spin alignment in the ordered state of each system is the same, along monoclinic [101], and thus the anisotropies are not orthogonal. Experience with other systems suggests the multicritical points tend not to occur in such cases. Since each component is ferromagnetic (though there is evidence that weaker antiferromagnetic interactions also operate) it seems unlikely that significant frustration, from strongly competing ferro- and antiferromagnetic interactions, will occur, thus making spin-glass behavior improbable. These expectations are fulfilled in the results that follow. Nevertheless, the mixture is an interesting one, since besides the randomness in site anisotropy there is also bond disorder, because of the different superexchange paths (Fe-S ··· S-Fe, Fe-S ··· Se-F, Fe-Se ··· Se-Fe) which will be present. We do in fact find a magnetic phase boundary, between paramagnetic and ferromagnetic states, of rather unusual shape, and such as has not been observed previously so far as we are aware.

II. EXPERIMENT

$\text{Fe}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$ and $\text{Fe}[\text{Se}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$ were prepared as described previously.^{15,18} Elemental analysis yielded results in excellent agreement (typically $\leq 1\%$ relative) with expected weight percents. Although a complete structure determination has not yet been performed on the diselenocarbamate (DSC) compound, preliminary single-crystal diffraction data indicate that this material is isomorphous to the dithiocarbamate (DTC). The unit-cell parameters and probable space group of $\text{Fe}[\text{Se}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$ have been found to be $a = 16.81 \text{ \AA}$, $b = 9.61 \text{ \AA}$, $c = 12.95 \text{ \AA}$, and $\beta = 120.1^\circ$, in $P2_1/c$ (C_{2h}^5 , monoclinic).¹⁹ Those of $\text{Fe}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$ have been reported to be $a = 16.43 \text{ \AA}$, $b = 9.42 \text{ \AA}$, $c = 12.85 \text{ \AA}$, and $\beta = 120.5^\circ$, in $P2_1/c$.²⁰ Thus the unit cell is about 5.2% larger in the diseleno than in the dithiocarbamate compound.

Solutions of various relative proportion were prepared by dissolving the desired amounts of each material in methylene chloride. Slow evaporation over a period of one week, under a flow of nitrogen gas and in the dark (to inhibit degradation of the slightly light-sensitive diselenocarbamate compound), produced homogeneous appearing polycrystalline material, but no single crystals large enough for magnetic measurements. X-ray diffraction patterns indicated that the mixtures were microscopically homogeneous at the level probed by this technique, with peak positions intermediate between those of the pure constituents. Sulfur and selenium concentrations were determined by atomic absorption spectrometry, and were typically within a few percent of the nominal composition. Analysis of different portions of a particular batch agreed to within 0.01 mole fraction unit.

Magnetization and susceptibility measurements were made using a variable temperature vibrating sample magnetometer system described previously.¹⁸ Data shown in the following have been corrected for demagnetization, and are considered to be accurate to $\pm 2\%$, with a pre-

cision much better than this. Temperatures were measured with a carbon-glass resistance thermometer located in immediate proximity to the sample, and are estimated to be accurate to $\pm 0.005\text{--}0.02 \text{ K}$, depending on the range. Magnetic field values are accurate to $\pm \max(2 \text{ G}, 0.1\%)$. The samples used were packed polycrystalline aggregates of approximately 100 mg, measured to 0.01 mg.

III. RESULTS AND ANALYSIS

The inverse molar susceptibility as a function of temperature is shown in Fig. 2 for an $x = 0.77$ polycrystalline sample of $\text{Fe}[\text{S}_{2x}\text{Se}_{2(1-x)}\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$. As is the case for other compositions, the data are quite linear to 20 K or less, but show a slight antiferromagnetic deviation (to larger χ^{-1}) at lower temperature. This is somewhat more pronounced for Se-rich mixtures than for S-rich. Weiss Θ values from Curie-Weiss fits, $\chi_M = C/(T - \Theta)$, to data in the linear regime are uniformly positive however, and are shown in Fig. 3, as are values determined from our measurements on the pure components.

The susceptibility is shown in more detail in Fig. 4, for lower temperatures and using an applied field of 20 G. From the extremely rapid increase of the susceptibility and the very large values attained below 5 K it is evident that a ferromagnetic transition is occurring. That the susceptibility does not level off to a constant demagnetization limited value is due to the polycrystalline nature of the sample. An inflection point in $\chi(T)$ occurs at $2.54 \pm 0.02 \text{ K}$. For a polycrystalline sample of $\text{Fe}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$ measured in a 20 G field, an inflection point occurred at $2.46 \pm 0.02 \text{ K}$, in excellent agreement with the previously determined transition temperature from single-crystal work, 2.458 K.¹⁶ In a polycrystalline sample of $\text{Fe}[\text{Se}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$ measured in a 20-G field a similar feature occurred at $3.47 \pm 0.03 \text{ K}$, agreeing well with the previously determined transition temperature from single-crystal work, 3.463 K.¹⁸ Thus it appears that inflection points in low-field $\chi(T)$ curves provide fairly good estimates of the transition temperatures in these systems, even though the data pertain to

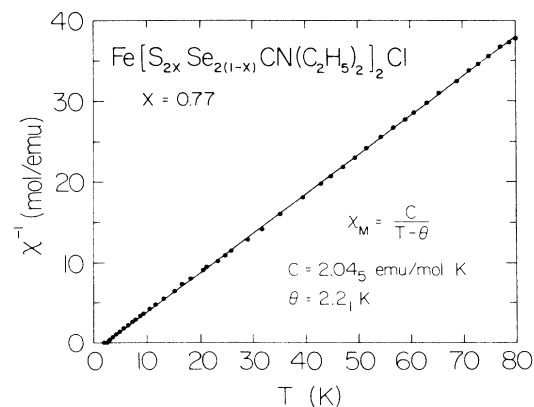


FIG. 2. Inverse molar susceptibility vs temperature for an $x = 0.77$ polycrystalline sample of $\text{Fe}[\text{S}_{2x}\text{Se}_{2(1-x)}\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$, and Curie-Weiss fit in the 20–80 K range.

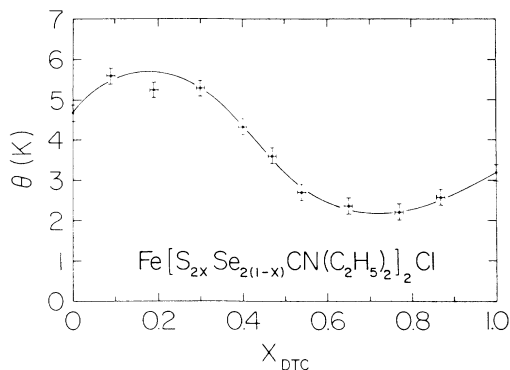


FIG. 3. Weiss Θ vs composition for polycrystalline $\text{Fe}[\text{S}_{2x}\text{Se}_{2(1-x)}\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$. Curve through data is only a guide to the eye.

polycrystalline material.

Low-field $\chi(T)$ curves for other mixtures were generally similar in appearance to that in Fig. 4 for $x = 0.77$. Inflection points were estimated and taken to be equal to $T_c \pm 0.02$ K. These are plotted as a function of composition to produce a magnetic phase diagram, Fig. 5. Its form will be discussed in the next section.

As an auxiliary approach to the determination of T_c in our samples, the method of Kouvel-Arrott plots was employed.²¹ Isotherms of M^2 versus H/M , where H is the internal field $H_{\text{app}} - NM$ (N was taken as $4\pi/3$ for our polycrystalline, approximately equidimensional samples), were constructed and analyzed for the $M = 0$ intercept, $(H/M)_0$, for a series of temperatures above T_c for each sample. An example appears in Fig. 6, for an $x = 0.30$ mixture. Since $(H/M)_0$ is the inverse initial susceptibility, which approaches 0 (infinite susceptibility) as T approaches T_c , an extrapolation to $(H/M)_0 = 0$ can be made in order to determine T_c . Such extrapolations for

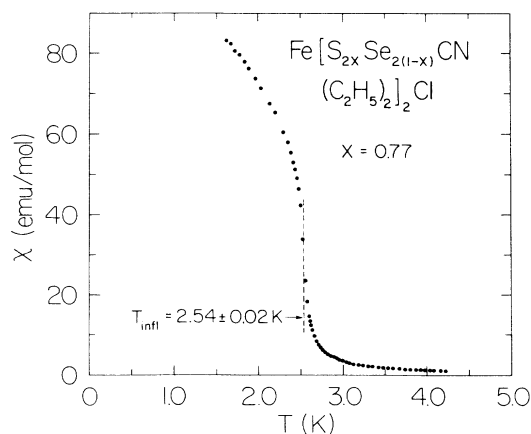


FIG. 4. Molar susceptibility vs temperature for an $x = 0.77$ polycrystalline sample of $\text{Fe}[\text{S}_{2x}\text{Se}_{2(1-x)}\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$ below 5.0 K, measured in a 20-G field. The inflection point in the data is also indicated.

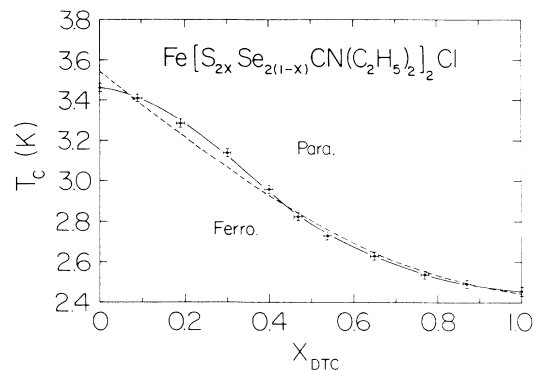


FIG. 5. Magnetic phase diagram of $\text{Fe}[\text{S}_{2x}\text{Se}_{2(1-x)}\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$. Solid curve through data is a guide to the eye. The dashed curve is a theoretical approximation described in the text.

several samples are shown in Fig. 7. It was found that the T_c values obtained by this method were systematically lower than those estimated from inflection points in $\chi(T)$ by from 0.05 to 0.08 K. We believe that this occurs because of the polycrystalline nature of the samples, in conjunction with the strong anisotropy of these materials. That is, an error in the observed sense (too low a T_c) can be attributed to a too-large value of H/M at any particular temperature and internal field, compared to what would be observed in a single-crystal easy axis measurement. That the differences between the Kouvel-Arrott and inflection-point estimates for T_c are very similar increases our confidence in this explanation, and indirectly in the accuracy of the inflection-point values.

IV. DISCUSSION

Each of the mixtures studied orders ferromagnetically, as expected from the behavior of the pure constituents.

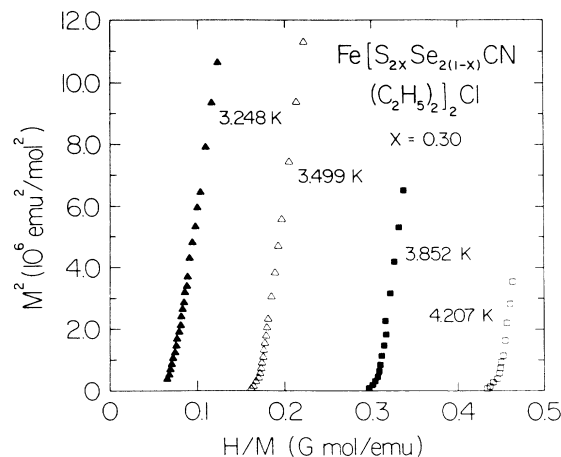


FIG. 6. Kouvel-Arrott plot for an $x = 0.30$ polycrystalline sample of $\text{Fe}[\text{S}_{2x}\text{Se}_{2(1-x)}\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$.

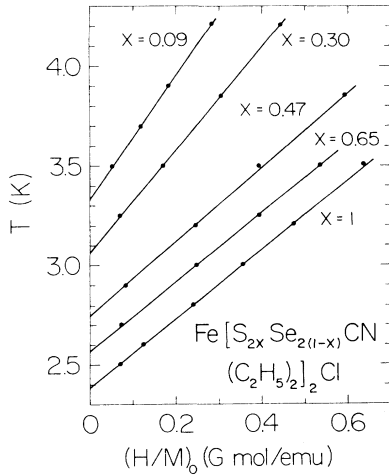


FIG. 7. Temperature vs inverse initial susceptibility, from Kouvel-Arrott plot, for several samples of $\text{Fe}[\text{S}_{2x}\text{Se}_{2(1-x)}\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$. Extrapolations to $(H/M)_0=0$ yield estimates for the critical temperatures.

But the variation of Θ and T_c with composition are each somewhat unusual. The wavelike appearance of $\Theta(x)$, Fig. 3, is unprecedented so far as we know, though the variation of the Weiss constant has rarely been reported in studies of mixed magnets. In mean-field theory Θ is, in general, a function of all exchange interactions that operate, whereas T_c can be a function of only a subset of these.²² This occurs typically in antiferromagnets. Each of the components of our mixed system is believed to be a canted ferromagnet, in which two inequivalent sublattices occur with sublattice magnetization vectors approximately 41° apart due to the constraints of crystal-field anisotropy. The crystal structure suggests that several different exchange pathways occur, both between and within sublattices. Measured Θ values for the pure systems, shown in Fig. 3, are somewhat larger than the respective ferromagnetic ordering temperatures, as is normally the case. Comparison of Figs. 3 and 5 reveals that while this remains the case for most of the compositions studied, in particular on the Se-rich side of the phase diagram, there is a region, $0.56 \leq x \leq 0.86$, where Θ is less than T_c . In ferromagnetic substances this is rare, and presumably indicates here the presence of substantial antiferromagnetic interactions, in addition to the dominant ferromagnetic interactions. The distribution of interactions can be assumed to depend upon the relative proportions of the two components; moreover, new interactions, along Fe-S . . . Se-Fe pathways, are introduced on mixing. It would appear that while the ferromagnetic interactions present still dominate the behavior, the influence of any antiferromagnetic interactions present is greatest in the region $0.56 \leq x \leq 0.86$.

A somewhat more detailed attempt can be made to account for the variation of T_c with x , Fig. 5. Thorpe and McGurn¹³ have studied the different kinds of magnetic phase diagrams that can occur in magnetic alloys with in-

teractions all of a given sign. A phase diagram classification scheme, based on the initial slopes of $T_c(x)$ at the extremes of the diagram, encompasses nine types of phase diagram, in addition to the simple mean-field theory result of a straight line connecting the transition temperatures of the pure constituents. The phase diagram we find, Fig. 5, is of type *S* (signifying a "straddle" of the mean-field line) in the classification scheme of Thorpe and McGurn. Their theory also makes predictions about the type of disorder, and the range of exchange interaction values J_{AA} , J_{BB} , and J_{AB} (the first two are pure system values, but may also apply between appropriate sites in the mixture; the third arises only in a site disordered mixture) necessary to yield a particular type of phase diagram. Bond disorder alone, in the restricted form with only two exchange parameters, is not favorable for realizing most of the possible phase diagram types, including *S* type diagrams. Site disorder, mainly because of the extra interaction parameter J_{AB} , leads to greater variety, especially in calculations beyond the mean-field level. *S*-type diagrams are predicted to occur for suitable joint parameter ranges. Details depend on the precise model employed, and some numerical results are given in Ref. 13 for honeycomb, square and $z=3$ Bethe lattices for $S=\frac{1}{2}$. The types of diagrams possible in these cases appear to be the same, and the parameter ranges (J_{AA} , J_{BB} , J_{AB}) over which the different types of diagram are favored are also quite similar.

It is anticipated that if interactions are not strongly competing (though, as mentioned, there probably are some antiferromagnetic interactions in our system) then the general form of the phase diagram will not be very different in three dimensions than in two dimensions. The parameter ranges over which a particular type of diagram is favored may of course depend upon dimensionality and other details. Perhaps a more serious problem in comparing our phase diagram with Thorpe and McGurn's theory, which assumes Ising model behavior, is that one component (*S*) is Ising-like while the other component (*Se*) is *XY*-like. However, there is a significant anisotropy in $\text{Fe}[\text{Se}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$ favoring the [101] direction,¹⁸ making it at least somewhat Ising-like, so that this difficulty in comparison may not be major.

Attempts were made to account for the observed phase boundary, Fig. 5, using the expression given in Ref. 13 for the Bethe lattice,

$$1 = (z-1)[x \tanh(\beta_c J_{AA}) + (1-x) \tanh(\beta_c J_{BB})] - \{(z-1)^2 x(1-x)[\tanh(\beta_c J_{AA}) \tanh(\beta_c J_{BB}) - \tanh^2(\beta_c J_{AB})]\}, \quad (1)$$

where $\beta_c = 1/kT_c$ and x is the concentration of component *A*. Five interacting neighbors ($z=5$) were assumed, as concluded previously. It may be noted that the same phase boundary can be obtained with different z values if the magnitudes of J_{AA} , J_{BB} , and J_{AB} are allowed to vary but their relative sizes remain the same. It was quickly ascertained that the observed *S*-shaped $T_c(x)$ could not be reproduced with any set of parameters that

were reasonably acceptable with respect to (1) yielding the pure component transition temperatures, and (2) providing a monotonic decrease of T_c with increasing x_{DTC} . This is presumably due to the limitations of the model (all interactions the same sign, Ising-Ising, two-dimensional) as applied to our system.

It was found, however, that the observed transition temperature, if not the S shape itself, could be fairly well reproduced, to within 0.08 K or so, by an appropriate set of exchange parameters. A formal best-fit set was found to be $J_{AA}/k = 0.624$ K, $J_{BB}/k = 0.906$ K and $J_{AB}/k = 0.658$ K. The S-rich side of the phase diagram is fit quite well, to within 0.03 K at worst. This seems consistent with the fact that the sulfur system is the more Ising-like component. The Se rich side of the phase diagram is fit less well, and the $x_{\text{DTC}} = 0$ transition temperature is 3.546 K, about 0.08 K above observation. One can adjust J_{BB} downward (and J_{AA} and J_{AB} slightly also) to fit $T_c = 3.463$ K for the pure selenium system much better, but this leads to a worsening of the general agreement on the Se-rich side, with some differences becoming as large as 0.12 K. The resulting J values are not very different from those given above in any case, and it seems evident that one cannot expect to do much better within

the limitations of the theory as applied to our system. The fitted curve appears dashed in Fig. 5. As noted, it is not of S type in Thorpe and McGurn's scheme, but rather of B type.

Comparison with previously determined average J values for the pure systems (from high temperature fitting on a true spin $S = \frac{3}{2}$ basis) requires scaling the above J values down substantially, by approximately $[\frac{3}{2}/\frac{1}{2}]^2$, since the theory applied is for spin $\frac{1}{2}$. The resulting values are substantially smaller than the mean $J/k = 0.16$ and 0.37 K determined previously for the sulfur and selenium systems, respectively.^{15,18} Presumably this is another indication of the limitations of the model as applied to our system. We hope that our experimental findings will provoke a more specific theoretical study of this interesting mixed magnetic system.

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