Monte Carlo study of the transition from a ferromagnet to a spin glass in Fe-Al alloys

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The transition from a ferromagnet to a spin glass in Fe-Al alloys as a function of Al concentration is studied by Monte Carlo methods. Following a model, initially proposed by Sato and Arrott, the spins on the Fe atom are assumed to interact via a direct ferromagnetic exchange between nearest neighbors and an antiferromagnetic superexchange between two Fe spins which are separated by an Al atom. These two interactions are sufficient to account qualitatively for the observed crossover from a ferrromagnet to a spin glass. This spin glass differs from the usual models, since the exchange constants are not random. Here the frustration arises only from the positional disorder of the Fe and Al atoms.

Recently, Shull, Okamoto, and Beck[1] studied the magnetic properties of Fe-Al solid solutions in two atomic crystal structures. They found that $Fe_{70}Al_{30}$ becomes ferromagnetic below $T_c = 400$ K, then becomes superparamagnetic on further cooling below $T_0 \approx 170$ K and finally freezes into a spin glass (or mictomagnetic) state below 92 K. They also found that the alloys $Fe_{70.5}Al_{29.5}$ to $Fe_{73}Al_{27}$ transform directly from a ferromagnet to a spin glass, while alloys with more than 30 at.% Al freeze into a spin-glass state directly from the paramagnetic phase. This crossover from ferromagnetism to spin-glass ordering proves that competing ferro- and antiferromagnetic interactions are present, as has been found in several other magnetic alloys,[2] e.g., PdMn and PdFeMn. However, in these two examples, the competing antiferromagnetic interaction is probably a result of direct nearest-neighbor exchange between two different types of magnetic atoms. This cannot be the case for Fe-Al alloys, since the Al atoms do not have a magnetic moment. These alloys also differ from the canonical spin-glass AuFe, since the Fe concentration is not dilute, and one expects the long-range Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction to be relatively unimportant.

Arrott and Sato[3] first found that the spontaneous magnetization in a 30.4 at.% Al alloy in the [FeAl]-ordered crystal structure (Cs-Cl structure) disappeared below 180 K. They[4] then proposed a simple model to account for this transition, which included a direct, ferromagnetic exchange between nearest-neighbor Fe atoms and an antiferromagnetic, superexchange between two Fe atoms, which were separated by an Al atom. Their original calculation suggested a transition from ferromagnetism to antiferromagnetism as a result of this indirect exchange interaction. However, neutron-diffraction[5] experiments found no evidence for long-range antiferromagnetism. The model also incorrectly predicted that the ordered $Fe_{50}Al_{50}$ alloy would be antiferromagnetic. It was, in fact, found to be paramagnetic down to the lowest temperatures measured.[6] Thus, the original predictions based on this model do not agree with the experimental results.

Shulka and Wortis,[7] however, have pointed out that an indirect exchange model does account for the spin-glass transition in these alloys. They have calculated, using real-space renormalization-group techniques, the phase diagram for a model containing an indirect exchange between Fe atoms. Their results agree reasonably well with the experimental results of Ref. 1, and show that the indirect-exchange model can explain the transition from a ferromagnet to a spin glass as the Al concentration is increased. The only difficulty remaining with this model is that it predicts an antiferromagnetic transition for the ordered $Fe_{50}Al_{50}$ alloy. This also can be corrected if one includes the measured reduction of the Fe magnetic moment due to the local Al environment.[8] One simple model, which gives qualitative agreement with the measured magnetic moment, is to assume the magnetic moment on an Fe atom vanishes whenever the number of Al nearest and next-nearest neighbors exceeds a critical value, taken to be six in a model for completely disordered $Fe_{1-x}Al_x$. Then, as the concentration of Al approaches 0.5, where each Fe is surrounded by 8 Al atoms, the system would be paramagnetic. This effect was also included in the calculations by Shulka and Wortis.[7]

The purpose of this paper is to study by Monte Carlo techniques the indirect exchange model originally proposed by Sato and Arrott[4] in the Al concentration range $0.25 < x < 0.50$. Here we consider a model system of Ising spins ($\sigma_i = 2S_i^z = \pm 1$) described by the Hamiltonian,

$$\mathcal{H} = -J_{NN} \sum_{NN} \sigma_i \sigma_j - J_{SE} \sum_{SE} \sigma_i \sigma_j \ , \qquad (1)$$

where the spins are situated on a bcc lattice with periodic boundary conditions. The spins are located at the Fe sites, while the Al sites have no spin. The first term in Eq. (1) is a ferromagnetic exchange $J_{NN}(>0)$ taken between all nearest-neighbor (NN) spins on the lattice. The second term is an indirect antiferromagnetic exchange $J_{SE}(<0)$, between two spins, separated by an Al atom (see Anderson[9] for a complete review of superexchange). This antiferromagnetic contribution breaks the long-range order which would ordinarily prevail due to the strong direct exchange. The values of J_{NN} and J_{SE} are taken as constants, with $\alpha \equiv -J_{SE}/J_{NN}$. This model differs slightly in detail from that used in Ref. 7, since in Eq. (1), I follow Sato and Arrott[4] and include an indirect exchange only between Fe atoms which are located at the body diagonals. Note that the exchange constants are not described by a distribution, as in the typical models of a spin glass.[10] However, it is similar to a model for insulating spin glasses recently proposed by Kinzel, Binder, and Stauffer[11] which has ferromagnetic NN and antiferromagnetic next-nearest-neighbor interactions.

$Fe_{1-x}Al_x$ solid solutions have either a [Fe_3Al]- or [FeAl]-type atomic order on a bcc lattice. The bcc lattice is divided into two sc lattices. One of these is occupied only by Fe atoms and will be denoted as sublattice I, while the second sc sublattice contains both Al and Fe atoms, and will be denoted sublattice II. In the [FeAl]-type atomic order, the Fe and Al atoms occupy the sublattice II randomly. In the [Fe_3Al]-ordered phase, sublattice II must further be divided into two fcc lattices. For the concentration range of interest, $0.25 < x < 0.50$, one of these fcc sublattices is made up of Al atoms, while the second contains Fe and Al atoms randomly distributed. Therefore, in the ferromagnetic $Fe_{75}Al_{25}$[Fe_3Al], there are three Fe and one Al fcc sublattices. Because of this ordering, only Fe atoms on the sublattice I interact via the indirect superexchange with a second Fe spin, located at the body diagonal. Those Fe atoms on sublattice II have only Fe atoms as nearest neighbor and therefore do not participate in the indirect exchange. Since the ordered $Fe_{75}Al_{25}$[Fe_3Al] configuration is known to be ferromagnetic, one is led to a useful constraint for the only free parameter of the model, $\alpha = -J_{SE}/J_{NN}$. In the ordered ferromagnetic phase, all the indirect bonds are frustrated, and the ground-state energy per spin is

$$E(0,\alpha)/J_{NN} = -\tfrac{1}{6}(16-8\alpha) \quad . \tag{2}$$

For $\alpha > 0.5$, this is no longer the lowest-energy state. It is an unusual antiferromagnetic ordering in which the spins on sublattice I have a period of four lattice spacings in all three spacial directions. The state is represented by a sequence of two up-spins, followed by two down-spins, etc. This state was found to have a second-order phase transition to the paramagnetic phase. This gives an upper limit for the ratio α of 0.50. In the calculations described below, we take $\alpha = 0.40$.

The simultations were carried out by the Monte Carlo method[12–15] in a cube, with periodic boundary conditions, containing $N = 2000$ sites. Since the Al atoms have no spin, some of these sites were vacant. We applied single spin-flip (Glauber) dynamics, over time intervals between 700–1000 Monte Carlo steps (MCS) per spin, at various temperatures and initial configurations at zero magnetic field. Besides the energy, magnetization, and staggered magnetization, the time-averaged[13] Edwards-Anderrson order parameter $q(t)$ was calculated to determine the spin glass ordering. The order parameter $q(t) = \overline{\langle \sigma_i \rangle^2}$ is defined as the configuration average over the square of the magnetization. Though $q(t)$ relaxes towards its equilibrium value very slowly,[15] and cannot be considered in equilibrium for the runs made here, it does indicate when spin-glass ordering has occurred. This is in the experimental sense, not in the sense of rigorous equilibrium in the thermodynamic limit.

The absolute value of the magnetization M for $x = 0.25$ for both the [Fe_3Al] and [FeAl] atomic ordering and for $x = 0.30$ in the [Fe_3Al] atomic order is shown in Fig. 1 for $\alpha = 0.4$. For the [Fe_3Al] atomic order, $Fe_{75}Al_{25}$ is completely ordered at $T = 0$, with the magnetization attaining its maximum value. For the other two cases, due to the disorder, the ordered $T = 0$ state has less than its maximum magnetization. Note that T_c is slightly larger for the [FeAl]

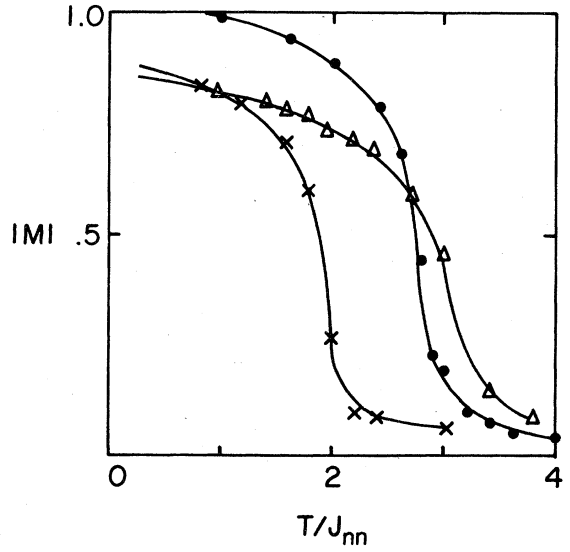

FIG. 1. Absolute value of the magnetization M versus T/J_{NN}. The solid circles are for $Fe_{75}Al_{25}$[Fe_3Al], crosses for $Fe_{70}Al_{30}$[Fe_3Al], and triangles for $Fe_{75}Al_{25}$[FeAl].

phase, than [Fe_3Al] for $x=0.25$. This differs from experimental results.[4] However, it is known that the Fe magnetic moment is slightly larger in the [Fe_3Al] structure than for the [FeAl] state, which accounts for this difference. The ferromagnetic phase extends to $x \approx 0.34$ for this model with $\alpha=0.4$. This differs from the experimental results mentioned above.

The system orders into a spin-glass state for $x \gtrsim 0.35$. In this regime, the magnetization vanishes, but $q(t)$ is nonzero, as shown in Fig. 2 for $x=0.35$. Figure 3 shows the specific heat obtained from $C=\partial E/\partial T$ for $x=0.35$. Note the rounded maximum characteristic of spin-glass ordering. There was some evidence for a transition from a paramagnet to ferromagnet to spin glass as the temperature is lowered for $x \approx 0.34$. For some spin configurations, M was found to decrease as the temperature was lowered, indicating a possible transition from a ferromagnet to a spin glass. In one case, M rose to a value of 0.3 at $T \sim 0.6 J_{NN}$, then fell to a value near 0.1 for $T \sim 0.2 J_{NN}$. The effect was reproducible upon cycling up and down in temperature. However, this effect was not seen in all the runs at the same concentration. The lattice is too small and available running time too short to study this transition in more detail. However, from runs at $x=0.33$ and 0.35, it can be concluded that, in this model, the concentration range over which a ferromagnetic to spin glass transition occurs is probably very narrow, $x \sim 0.34 \pm 0.01$. There was no evidence for a transition from a ferromagnet to superparamagnet to spin glass as was found experimentally for $Fe_{70}Al_{30}$[Fe_3Al].

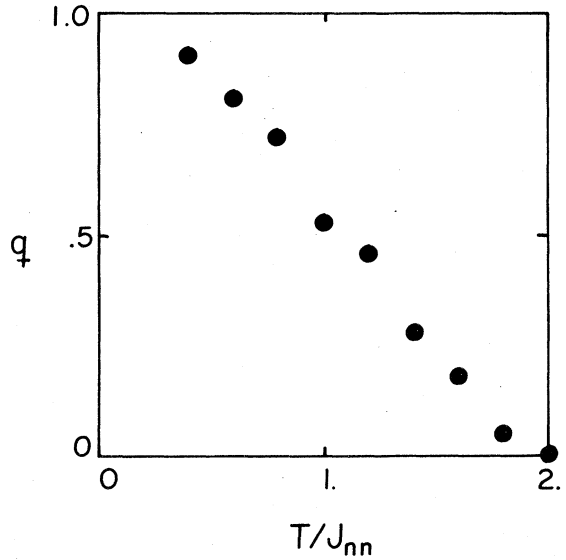

FIG. 2. Temperature variation of the Edwards-Anderson order parameter $q=\overline{\langle\sigma_i\rangle^2}$ after 800 MCS/spin for $Fe_{65}Al_{35}$[Fe_3Al] for a 2000-site lattice.

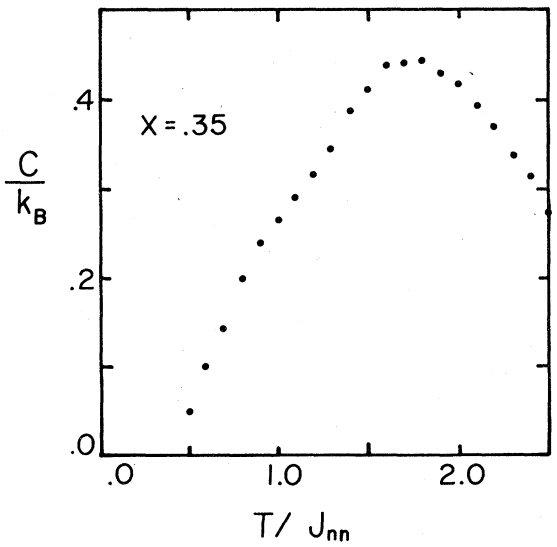

FIG. 3. Specific heat plotted vs temperature for $x=0.35$. Data obtained via $C=\partial E/\partial T$.

An approximate phase diagram for the [Fe_3Al] atomic order for $J_{SE}/J_{NN}=-0.4$ is shown in Fig. 4. Results for [FeAl] order are similar, with transition temperatures typically 10% higher. For $x \gtrsim 0.44$, this model would predict a crossover from spin glass to antiferromagnetic order. This occurs for $x \to 0.5$, since the number of NN Fe atoms goes to zero and the indirect exchange gives rise to an antiferromagnetic ordering on sublattice I. This is not seen experimentally. However, one important experimental effect has not been included. This is the dilution of the Fe magnetic moment due to the local Al environment. One simple model, known as the local environment model, was proposed in Ref. 8 to account for this effect in disordered Fe-Al alloys. In this model, an Fe atom has no magnetic moment when the number of nearest- and next-nearest-neighbor Al atoms exceeds a critical value n_c, assumed[8] to be six for disordered $Fe_{1-x}Al_x$ alloys. A more realistic model would be to vary the magnetic moment continuously with the local Al environment. In either case, the effect of the dilution is to eliminate the unwanted antiferromagnetic transition for $Fe_{50}Al_{50}$. I have considered the cases $n_c=7$ and 8. For $n_c=7$, the system orders into a ferromagnetic state for $x \gtrsim 0.43$, with a transition temperature T_c which vanishes as $x \to 0.50$. For $n_c=8$, as shown in Fig. 4, one has only spin-glass ordering with $T_{SG} \to 0$ as $x \to 0.50$, as found experimentally. The results are expected to be similar for a more realistic model in which the size of the magnetic moment is varied continuously with the Al environment.

As seen from Figure 4, this simple Ising model with indirect exchange reproduces many of the quali-

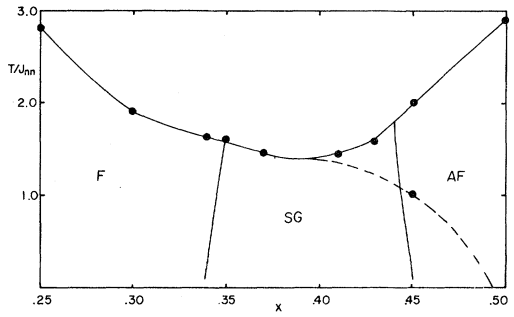

FIG. 4. Solid curve is approximate phase diagram for $Fe_{1-x}Al_x$ [Fe_3Al] for $0.25 < x < 0.50$ and $\alpha = 0.40$. F indicates a ferromagnetic state, SG the spin glass, and AF the antiferromagnetic state. The dashed curve is the phase diagram if the reduction in Fe magnetic moment caused by the local Al environment is included, with $n_c = 8$. The closed circles correspond to the concentrations at which the simulations were performed.

tative features of the experimental results for Fe-Al alloys. This model predicts that the transition from a ferromagnet to a spin glass does not occur until $x \approx 0.34$, while it is found experimentally to be as small as 0.27. Since the ratio of the couplings α is constrained to be less than 0.50, this concentration can not be changed appreciably by increasing α further. The concentration of this crossover can be understood in terms of frustration model of spin glasses. For $0.33 \leq \alpha \leq 0.6$, Fe atoms with six or more nearest neighbor Al atoms are frustrated in a completely ordered ferromagnetic state. For $x = 0.34$, this amounts to roughly 34% of the Fe atoms. At concentrations greater than this, the system prefers to order into a random spin-glass state.

The differences between this calculation and the experimental results can probably be attributed to (i) use of Ising instead of Heisenberg spins and (ii) the oversimplified manner in which superexchange was included. In a realistic model of superexchange, particularly for these random alloys, probably not all Fe atoms with an intermediate Al atom interact and if so not always with the same strength. This additional randomness would improve the agreement with the experimental results in two ways. First, the value of α could be increased beyond 0.5, without an ordered antiferromagnetic phase becoming stable at $x = 0.5$. This would reduce the critical concentration for spin-glass ordering, more in line with the experiment. Second, one could use a more realistic value for $n_c = 6$ or 7 instead of the value 8 used here. Since this would introduce several additional free parameters which are not well known microscopically, a generalization of the original model will not be considered here. However, it is satisfying to see that this simple model, first proposed before spin glasses were ever discussed, works so well. This system is of particular interest, because it is a concentrated alloy, in which RKKY interactions should not be important. The spin-glass ordering occurs not as a result of random exchange constants, but instead, from the random positional disorder of the two atomic constituents.

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