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# Magnetic properties of cobalt and manganese aluminosilicate glasses

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Susceptibility measurements over a wide range of temperatures on concentrated amorphous transition-metal aluminosilicate glasses (11.8–33.5-at.% Co, 12.3–41.7-at.% Mn) are reported. In the high-temperature regime ($> \sim 50$ K), these glasses show Curie-Weiss behavior with large negative paramagnetic Curie temperatures, indicating the presence of strong antiferromagnetic exchange interactions. The slope of $\chi^{-1}$ vs $T$ curves shows a slight dependence on the transition-metal concentration, implying that the local environment of the magnetic ions is concentration dependent. The magnitude as well as the concentration dependence of the magnetic moments, as determined from the high-temperature data, can be understood for the cobalt glasses by appealing to the solidus surface diagram (which gives information concerning the local environment of the cobalt ions) of the glass system. In the low-temperature regime ($1 < T < 50$ K), the susceptibility of both systems is enhanced and furthermore exhibits an anomalously sharp peak below $\sim 10$ K. The magnitude of this peak decreases with increasing magnetic-ion concentration, while the position at which it occurs shifts to higher temperatures. This low-temperature behavior can be explained satisfactorily by assuming that these glasses contain small ($\sim 50$ Å) regions of relatively high cobalt or manganese concentration (monodomains) which are ordered antiferromagnetically, and which are separated from one another by paramagnetic areas of lesser magnetic-ion content. Each monodomain has a net magnetic moment which freezes in the direction of its anisotropy field at the so-called blocking temperature, giving rise to the peak in the susceptibility. By calculating the susceptibility of the monodomains and properly averaging over the random directions of their anisotropy fields, remarkable agreement with the low-temperature data is obtained. The values of the anisotropy constants needed to fit the data are consistent with values found in various cobalt and manganese compounds.

## INTRODUCTION AND CONCLUSION

In 1965, Schinkel and Rathenau measured the magnetic susceptibility of a series of manganese-oxide borate glasses.[1] These measurements showed that this glass system exhibits strong antiferromagnetic interactions, though no distinct antiferromagnetic transition was observed. Since then, a number of different glass systems as well as amorphous thin films have been studied with many of them showing dominant antiferromagnetic interactions. These systems include the chromium phosphate glass system,[2] as well as the iron, manganese, and vanadium phosphate glass systems,[3] and yttrium-iron thin films.[4] All of these systems show a remarkable similarity in their observed magnetic behavior. In the high-temperature region (i.e., for temperatures greater than about 50 K) all of the systems obey a Curie-Weiss law, with measurement extending as high as 600 K in some cases. In the low-temperature region, they all deviate from the linear Curie-Weiss behavior, exhibiting a strongly enhanced paramagnetism. Another feature which is common to all of the glasses studied thus far is the fact that the extrapolation of the linear portion of the $1/\chi$-vs-$T$ curve intersects the negative-temperature axis, implying that the dominant magnetic interactions are of an antiferromagnetic or ferrimagnetic nature. Such studies are of great interest since they may shed light on the question of whether or not magnetic ordering can occur in a system of randomly distributed interacting magnetic moments. It is the purpose of the present paper to describe and interpret the magnetic properties of concentrated transition-metal aluminosilicate glasses.

We have measured the susceptibility of several cobalt and manganese aluminosilicate glasses using a low-field (~ 5 G) ac mutual-inductance technique (500 Hz). The experimental procedures and results will be described in Sec. II. We find that at high temperatures these glasses also show a Curie-Weiss behavior. However, the slope of the $1/\chi$-vs-$T$ curves depends on the cobalt and manganese concentration, indicating that the magnitude of the magnetic moments depends on the magnetic-ion concentration of these glasses. This in turn implies that the crystal field at the site of the various magnetic moments varies with concentration. We have been able to account for the concentration dependence of the magnetic moment of the cobalt ion by making use of the solidus surface diagram for this system as well as of the known magnetic moment for the cobalt ion in various cobalt compounds.

TABLE I. Batch compositions of samples used in present work.

| Molar % | | | | Atomic % | |
|---|---|---|---|---|---|
| CoO | MnO | $Al_2O_3$ | $SiO_2$ | Co | Mn |
| 40.0 | | 40.0 | 20.0 | 11.8 | |
| 50.0 | | 30.0 | 20.0 | 16.1 | |
| 53.0 | | 32.4 | 14.6 | 17.0 | |
| 60.0 | | 30.0 | 10.0 | 20.0 | |
| 71.2 | | 23.7 | 5.1 | 25.8 | |
| 83.1 | | 15.5 | 1.4 | 33.5 | |
| | 35.0 | 10.0 | 55.0 | | 12.3 |
| | 40.0 | 10.0 | 50.0 | | 14.3 |
| | 50.0 | 5.0 | 45.0 | | 19.2 |
| | 60.0 | 10.0 | 30.0 | | 23.1 |
| | 70.0 | 5.0 | 25.0 | | 29.2 |
| | 80.0 | 5.0 | 15.0 | | 34.8 |
| | 90.0 | 3.0 | 7.0 | | 41.7 |

We have therefore shown that the high-temperature susceptibility provides a means to obtain information concerning the structure of the cobalt glasses in the immediate vicinity of the cobalt ions. A similar analysis for the manganese glasses has not been possible since the solidus surface diagram for this system is not available. Details will be provided in Sec. III.

At low temperatures, the susceptibility deviates dramatically from the linear Curie-Weiss behavior and displays a relatively sharp maximum at temperatures ranging from 2 to 8 K. This peaked behavior is to date unique in the studies which have been made on such glasses. It is tempting to assume that these glasses undergo a transition to a long-range antiferromagnetically ordered state. Although several molecular-field theories of amorphous antiferromagnetism have been proposed,[5] none of these have developed far enough to permit a meaningful comparison with the experimental data. However, in the present paper we have taken a different point of view, and have asked the question whether it is possible to account for the low-temperature data without assuming the existance of long-range antiferromagnetic order. Significantly enough, this question can be answered in the affirmative, as will be shown in Sec. IV. The shape of the peaks in the low-temperature susceptibility are strikingly similar to the susceptibility of small magnetic particles. It is this similarity which leads us to assume that our glass samples are inhomogeneous and consist of small regions (or monodomains)[6] of relatively high cobalt or manganese concentration separated from one another by less concentrated areas. By assuming that the monodomains are antiferromagnetically ordered owing to strong intradomain superexchange interactions, and subsequently employing Néel's model of small magnetic particles,[7] we have succeeded in explaining quantitatively our low-temperature observations.

## II. EXPERIMENTAL PROCEDURE AND RESULTS

### A. Glass preparation

The glass samples used in this study are formed by firing appropriate batch mixtures of reagent-grade aluminum oxide and cobalt or manganese carbonate with pure silica sand in a carbon-arc-image furnace. In this process, the metal carbonate is converted to the metal oxide by dissociation. The chemicals were weighed out in proportions which would yield final compositions which were high in cobalt or manganese content. A listing of the compositions which formed good glasses and were subsequently studied is given in Table I. It was found that compositions with lower than about 40 wt.% metal oxide do not form glasses at all, which has also been observed by other investigators.[8]

The well mixed ingredients were placed in a refractory clay crucible and fired in air for 30 min–1 h. Several attempts to use recrystallized alumina crucibles failed as they cracked during the firing process, probably owing to large thermal gradients. After firing, the melt was quenched by one of three methods: (i) pouring into an aluminum mold to produce regular shaped slugs, (ii) pouring onto a copper plate to produce small beads, or (iii) allowing the melt to cool in the crucible itself. Comparison of x-ray data as well as magnetic properties showed no discernable differences in samples of the same batch composition quenched by these techniques. The melt was then divided to provide specimens for x-ray analysis, electron microscopy, and the magnetic measurements.

### B. X-ray analysis and electron microscopy

The specimens provided for x-ray analysis were powdered and examined with both a Wolf-Scherrer powder pattern camera and a Siemens x-ray diffraction unit. Neither method showed any evidence whatever of crystalline material in the glass samples quenched as above. This is not to say that such crystalline material could not be present, but only that any crystallites present were in quantities and/or particle sizes which were too small to be observed by these techniques. While an upper limit on the particle size is difficult to estimate, similar x-ray methods claim that the absence of x-ray diffraction maxima indicate that less than 0.1 wt.% of material is present with particle sizes greater than 500 Å.[9]

The samples were also annealed in an attempt to relieve the internal strains which were present owing to the quenching process. For various annealing temperatures up to 550°C and annealing times up to 12 h, it was found that the magnetic properties were unchanged. X-ray analysis of these annealed glasses also showed no devitrification. It was only after annealing temperatures greater than 650 °C were used that devitrification was evident in the samples.

The samples were also examined by means of electron microscopy for evidence of phase separation. The microscopy was done on direct platinum-carbon replicas obtained from fracture surfaces etched for 30 sec in a 1% HF solution. A Philips 100-keV (model E. M. 300) electron microscope was used to examine all of the replicas. In examining these replicas, it was found that the surface detail was essentially uniform over a given sample. There was no evidence of crystallites on these etched surfaces.

All of the samples quenched in the above manner showed some signs of liquid-liquid immiscibility with the 33.5-at.% cobalt sample showing the greatest extent of this phase separation. The electron micrograph for the sample shows very clearly one phase consisting of spherically shaped globules surrounded by a second phase. The average diameter of these spheroids was ~1000 Å. The fact that the globules are spherical implies that this phase is amorphous because, if it were predominately crystalline, the globules would develop as angular irregularly shaped particles. The electron micrographs which were made for the other samples show that the phase separation is not as well defined as for the 33.5-at.% sample. The phase-separated regions were on the order of 500–1000 Å in diameter with some as large as 2500 Å. It should be noted that, while electron microscopy shows clear evidence of phase separation, no analytical method is available to us to determine the exact composition of either phase.

### C. Magnetic measurements

The magnetic susceptibility measurements were made over the temperature range 1.5–300 K using a low-field ac mutual-inductance bridge apparatus designed after Maxwell.[10] The measuring frequency used was 500 Hz, and the peak value of the magnetic field was 5 G. In making these measurements, several different experimental procedures were followed. For the lowest temperatures (1.5 – ~20 K), the measurements were made by placing the sample in the measuring coil and then slowly [~1 K/(3–5 min)] drifting through this temperature range. In order to calculate the susceptibility using this technique, it is necessary to measure the response of the empty coil and make the appropriate subtractions. The advantage of this method is the fact that the response of the measuring coil to changes in the temperature is very predictable. Another advantage lies in the fact that the drift rate is slow enough to be considered isothermal; so a detailed examination of a sample's low-temperature behavior can be made. In the higher temperature region (20–300 K), a temperature regulation apparatus was used to stabilize the temperature of the sample and measuring coil before a measurement was made. Typical data taken in this manner for the glass samples are shown in Figs. 1–4. The susceptibility of the glasses appears to follow a Curie-Weiss-type behavior over a significant portion of the temperature range, with a marked deviation from this behavior noted for all samples at ~50 K, as seen in Figs. 1 and 2. From the linear portion of the $1/\chi$-vs-$T$ plots, the effective moments were calculated as well as the paramagnetic Curie temperatures. These values are listed in Table II. The apparent composition dependence of the effective moments will be discussed in detail in Sec. III.

At low temperatures the susceptibility displays a maximum, as may be seen in Figs. 3 and 4. The peak temperatures are listed in Table II. These data show several general trends in the low-temperature behavior as a function of the magnetic-ion concentration. With decreasing concentration, one notices that the maximum value of the susceptibility becomes larger and shifts to a lower temperature. Furthermore, the width of the susceptibility peak becomes distinctly smaller. The significance of these observations as well as the deviation from the Curie-Weiss behavior will be discussed in Sec. IV.

## III. DISCUSSION–HIGH-TEMPERATURE REGIME

As mentioned in Sec. II, the magnetic behavior of the cobalt and manganese aluminosilicate-glass systems can conveniently be described by considering two distinct temperature regimes. At high temperatures, the systems obey the Curie-Weiss law, while for lower temperatures a more complicated behavior is observed. In this section, we will give a complete discussion of the high-temperature susceptibilities.

From 50 to 300 K, the reciprocal susceptibility is accurately proportional to $T$, as seen in Figs. 1 and 2. The extrapolation of the linear portion of the $1/\chi$-vs-$T$ plots intersects the negative temperature axis, implying that the dominant magnetic interactions within the glasses are antiferromagnetic. The negative values of the paramagnetic Curie temperature $\theta$ also imply that, should any ordering take place, it would likely be of an antiferromagnetic or ferrimagnetic nature.

The measured paramagnetic Curie temperatures did not seem to show an explicit dependence on the concentration of the magnetic ions in the samples. They, however, differed from sample to sample, indicating that the observed magnetic behavior is not

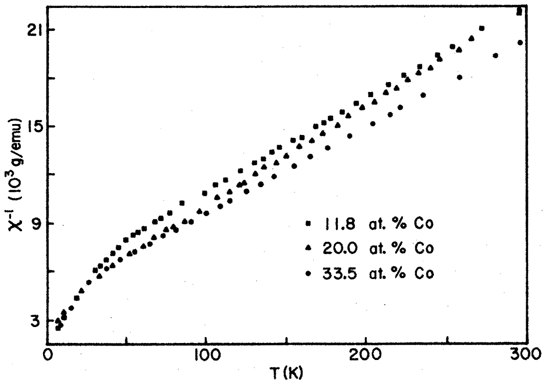

FIG. 1. Reciprocal susceptibility vs temperature for several cobalt aluminosilicate glasses.

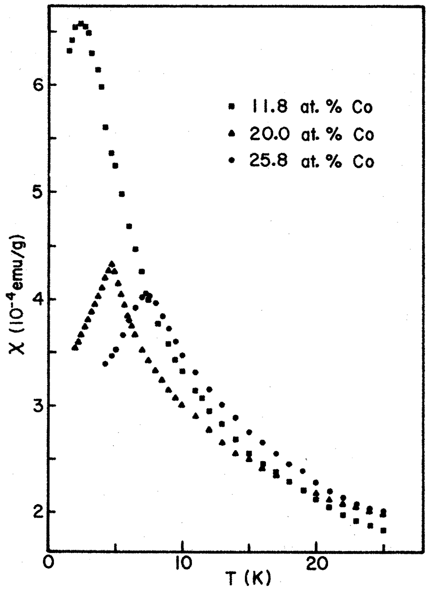

FIG. 3. Low-temperature susceptibility vs temperature for several cobalt aluminosilicate glasses.

due to the presence of microcrystalline material which could not be detected by means of x-ray analysis. If the observed magnetic behavior were due to microcrystalline material, all of the paramagnetic Curie temperatures would be the same.[11]

The second and more important quantity which can be determined from the high-temperature data is the ionic effective magnetic moment. This quantity is calculated from the measured slope of the linear portion of the $1/\chi$-vs-$T$ curve. The calculated effective moments for the cobalt glasses are plotted vs Co concentration in Fig. 5. This figure reveals a very noticeable trend in the magnitude of the effective moment as a function of composition. The lowest concentration glasses have the highest measured effective moments, with the magnitude of the moment decreasing for increasing Co content. The values of these effective moments range from a high of $6.73\mu_B$ for the 11.8-at.% glass to a low of $4.78\mu_B$ for the 33.5-at.% glass. There is also a noticeable break in the curve between 60- and 65-wt.% CoO. The significance of these data lies in the fact that this magnetic information can be used to make some definitive statements about the structure of the various glass concentrations.

In Fig. 6 is shown the solidus surface diagram for the cobalt-oxide aluminosilicate system.[12] This diagram was obtained by intentionally devitrifying glasses of different compositions and examining the resultant materials for crystalline content. In the various regions on the diagram, the compounds are listed according to their relative abundance. The points shown on the diagram indicate the composition of the cobalt glasses investigated in the present work.

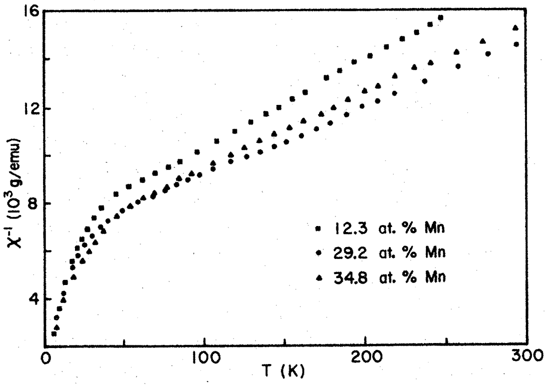

FIG. 2. Reciprocal susceptibility vs temperature for several manganese aluminosilicate glasses.

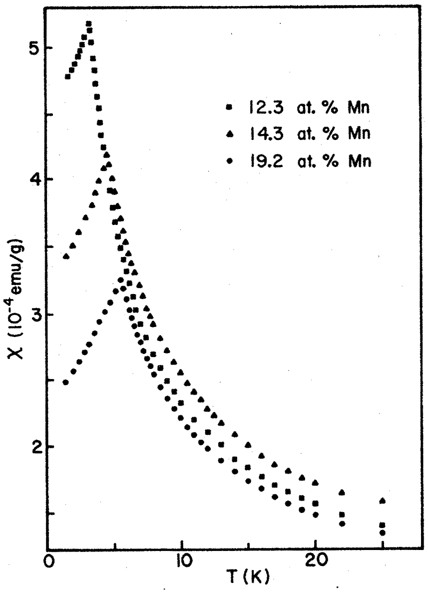

FIG. 4. Low-temperature susceptibility vs temperature for several manganese aluminosilicate glasses.

TABLE II. Magnetic-susceptibility data.

| | Magnetic-ion concentration (Atomic %) | Peak temperature (K) | Effective Moment ($\mu_B$) | Paramagnetic Curie temperature (K) |
|---|---|---|---|---|
| Co | 11.8 | 2.5 | 6.7 | −95 |
| | 16.1 | 2.3 | 6.0 | −90 |
| | 17.0 | 5.25 | 5.5 | −88 |
| | 20.0 | 4.75 | 5.1 | −66 |
| | 25.8 | 7.25 | 4.9 | −77 |
| | 33.5 | 7.8 | 4.8 | −84 |
| Mn | 12.3 | 3.3 | 6.96 | −194 |
| | 14.3 | 4.6 | 6.89 | −194 |
| | 19.2 | 5.55 | 6.01 | −245 |
| | 23.1 | 5.8 | 4.69 | −226 |
| | 29.2 | 6.15 | 4.85 | −210 |
| | 34.8 | 5.1 | 5.20 | −236 |
| | 41.7 | 6.5 | 5.37 | −224 |

It should be noted that the glasses fall into two distinct regions on the crystalline phase diagram. The dividing line between these regions is a line which extends from 30.1-at.% to $\sim$8.8-at.% Co (70-wt.% CoO to $\sim$40-wt.% CoO), with the $Al_2O_3$ content ranging from 0 to $\sim$60 wt.%. The point of intersection of this dividing line and a line which is drawn approximately through the points corresponding to our glass samples occurs at $\sim$24-at.% Co. This fact indicates that the break in the effective moment curve (i.e., Fig. 5) is due to a change in the local environment of the cobalt atoms. This change is due to the preference for dissimilar local order on either side of the dividing line of Fig. 6.

In the high-concentration glasses, i.e., those which are closer to the CoO vertex of the phase diagram and are thus below the dividing line of Fig. 6, one would expect that the local environment of the $Co^{2+}$ ions is very similar to that found in CoO or $Co_2SiO_4$. Therefore the magnetic moments for the glasses in this concentration region should be comparable to the moments found in these crystalline compounds. This is a result of the fact that the magnitude of the magnetic moment is determined primarily by the bonding symmetry of the $Co^{2+}$ ions. The measured values for the magnetic moments of $Co^{2+}$ in CoO and $Co_2SiO_4$ are $4.8\mu_B$ and $4.87\mu_B$, respectively.[13,14] As may be seen in Fig. 5, the effective moment for the high-composition glasses approaches $4.8\mu_B$ as the Co concentration increases. This seems to confirm the assumption made concerning the local environment and its influence on the effective magnetic moment.

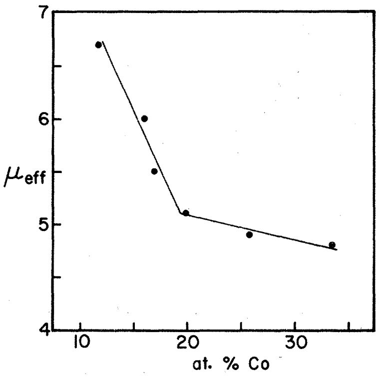

FIG. 5. Effective moment vs cobalt concentration.

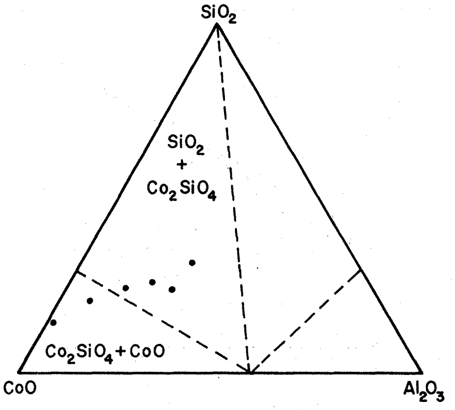

FIG. 6. Solidus surface diagram for the CoO • $Al_2O_3$ • $SiO_2$ system (Ref. 12).

In order to explain the unexpectedly high effective moment for the low-concentration glasses, we follow the same procedure. In the low-composition region of Fig. 6, it is noted that the dominant crystalline compounds are $SiO_2$ and $Co_2SiO_4$. It is possible that in the glass the excess silica changes the local order near the Co ions from one which resembles the local order found in $Co_2SiO_4$ to one which is similar to $CoSiO_3$. This latter compound is a chain silicate which in bulk form is antiferromagnetic with a transition temperature of 50 K and an effective ionic moment of $6.3\mu_B$.[15] Comparison of this moment with that found for the low-concentration cobalt glasses leads to the conclusion that the local order for these concentrations is similar to that found in $CoSiO_3$.

Thus the model which emerges for the explanation of the high-temperature magnetic data is one of a local order at the site of the cobalt atoms which is concentration dependent. For the lowest-concentration glasses, the local order is similar to that found in cobalt metasilicate ($CoSiO_3$), while for high concentrations this local order takes on the characteristics of cobalt oxide and cobalt orthosilicate ($Co_2SiO_4$). For the intermediate compositions, it is assumed that some mixture of these different types of local order occurs. The difficulty in trying to assign a particular structure to any specific composition lies in the fact that all samples displayed some evidence of liquid-liquid immiscibility, which makes the exact composition determination for the cobalt-rich and -lean phases impossible.

For the Mn aluminosilicates a similar analysis of the effective ionic moments cannot be made since the solidus surface diagram of this system is not available. Also, it has been reported that the Mn moments in manganese ortho- and metasilicate are nearly equal.[14–16] One would expect that local order corresponding to the known valence states of Mn is present in these glasses, and that therefore the susceptibility represents a weighted average over the different moments of these states. However, the experimental values of the effective Mn moments reported here range from $4.7\mu_B$ to $6.96\mu_B$ (see Table II), whereas the expected values for $Mn^{2+}$, $Mn^{3+}$, and $Mn^{4+}$ are $5.92\mu_B$, $4.9\mu_B$, and $3.87\mu_B$,[13] respectively. Therefore, the experimentally determined moments cannot be explained in terms of such a weighted average. This is particularly true for the moments which are greater than $\sim 6\mu_B$. No satisfactory explanation for these anomalously high moments is available.

## IV. DISCUSSION–LOW-TEMPERATURE REGIME

In the low-temperature regime (i.e., $T \lesssim 50$ K) there are several experimentally observed phenomena which must be analyzed: (i) deviation from the Curie-Weiss paramagnetic behavior, (ii) presence of a sharp susceptibility maximum at low $T$ ($T < 10$ K), and (iii) position, shape, and concentration dependence of the susceptibility maxima.

As was mentioned in the Introduction, the appearance of relatively sharp low temperature peaks in the susceptibility might indicate the onset of long-range antiferromagnetic order. However, at present there is not sufficient experimental evidence[11] or theoretical justification for the occurrence of a magnetically ordered state in the magnetic aluminosilicate glasses described in this paper. Instead of pursuing the question of whether or not an ordered magnetic state is possible at all in a structurally disordered glass, we have preferred to take a different point of view and have capitalized on the similarity (see below) of our experimental susceptibility curves and the predictions of Néel's theory of small magnetic particles.[7]

In 1952 Néel considered the behavior of small magnetic particles, which order magnetically below a certain ordering temperature $T_c$, where $T_c$ is approximately equal to the ordering temperature of the corresponding bulk material. In this paper we shall only be concerned with the case of antiferromagnetic order. A small antiferromagnetic particle develops a net magnetic moment due to an imperfect compensation of the ionic moments. In practice this net magnetic moment is large and often on the order of $100\mu_B$. An important ingredient of Néel's theory is the anisotropy energy of the particle. For simplicity we shall assume the anisotropy to be uniaxial, the anisotropy field being in the direction of a unit vector $\vec{u}$. If the anisotropy energy per unit volume is denoted by $K$, then the energy of a particle with magnetic moment $\vec{\mu}$ in the presence of a magnetic field $\vec{H}$ can be written

$$E = KV\sin^2\beta - \mu H\cos\theta \quad , \tag{1}$$

where $V$ is the volume of the particle, $\beta$ is the angle between $\vec{\mu}$ and $\vec{u}$, and $\theta$ is the angle between $\vec{\mu}$ and $\vec{H}$. Another essential quantity is the relaxation time

$$\tau = \tau_0 e^{KV/kT} \quad , \tag{2}$$

which represents the time required for the magnetic moment of the particle to reach thermal equilibrium. An interesting situation arises if $\tau$ is greater than the time of a measurement.[17] In that case, the magnetic moment will not be able to reach thermal equilibrium and will freeze in the direction of the anisotropy axis below a temperature on the order of $KV/k$. This temperature is called the blocking temperature, and will be denoted by $T_b$. Of course, for this effect to occur, $T_c$ must be greater than $T_b$, so the particle has a net magnetic moment in the first place. As a consequence, the susceptibility of the particle will be a maximum in the neighborhood of $T_b$. To calculate this effect, we adopt the following procedure. In thermal equilibrium the susceptibility of a particle with a large magnetic moment would be given by

$$\chi_{\text{equil.}} = \frac{d}{dH}\left(\frac{M(0)}{Z}\int_0^{\pi} d\theta \int_0^{2\pi} d\phi\, e^{-E/kT}\cos\theta\,\sin\theta\right) \quad , \tag{3}$$

where $Z$ is the classical partition function and $M(0)$ is the magnetization at $T = 0$ K. In order to take the freezing of the magnetic moment into account, we must restrict the motion of $\vec{\mu}$ and force it to point nearly in the direction of $\vec{u}$ or $-\vec{u}$ at all times. To that end we choose the $z$ direction along $\vec{u}$, take $\beta$ as the independent variable, and split the integration over $\beta$ into two parts. In the first integral $\beta$ shall vary from 0 to $\pi/2$, while in the second $\beta$ is confined between $\pi/2$ and $\pi$. The susceptibility of the particle then becomes

$$\chi = \frac{d}{dH}\left(\frac{M(0)}{I_1}\int_0^{2\pi} d\phi \int_0^{\pi/2} d\beta\, e^{-E/kT}\cos\theta\,\sin\beta + \frac{M(0)}{I_2}\int_0^{2\pi} d\phi \int_{\pi/2}^{\pi} d\beta\, e^{-E/kT}\cos\theta\,\sin\beta\right) \quad , \tag{4}$$

where

$$I_1 = \int_0^{2\pi} d\phi \int_0^{\pi/2} d\beta\, e^{-E/kT}\sin\beta$$

and (5)

$$I_2 = \int_0^{2\pi} d\phi \int_{\pi/2}^{\pi} d\beta\, e^{-E/kT}\sin\beta \quad .$$

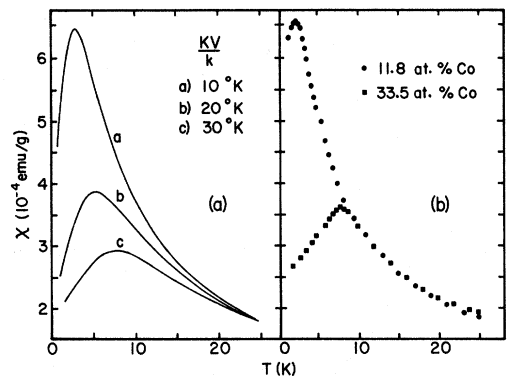

FIG. 7. Susceptibility vs temperature: (a) theoretical curves for several values of the anisotropy parameter $KV/k$; (b) 11.8-at.%- and 33.5-at.%-cobalt aluminosilicate glasses.

The angles $\beta$ and $\theta$ are related by the identity

$$\cos\theta = \sin\phi \sin\beta \sin\alpha + \cos\alpha \cos\beta \ , \tag{6}$$

where $\alpha$ is the angle between $\vec{u}$ and $\vec{H}$. We have evaluated $\chi$ numerically for various values of the parameter $KV/k$. In addition, an integration over $\alpha$ was performed to take into account the randomness of the anisotropy direction. The results of this calculation are shown in Fig. 7(a).

The striking similarity between the curves in Fig. 7(a) and our experimental data, as displayed in Fig. 7(b), has led us to the monodomain model of the transition-metal aluminosilicate glasses. This model assumes that these glasses consist of regions (i.e., monodomains)$^6$ of relatively high cobalt or manganese concentration separated from one another by areas of lesser magnetic-ion content. The magnetic moments within the monodomains are assumed to order antiferromagnetically well above the blocking temperature because of strong intradomain superexchange interactions. We wish to emphasize here that we in no way think of these monodomains as small crystallites, but rather assume them to be truly amorphous.$^{18}$ In order to estimate the susceptibility of such a system, we neglect the contribution of the interdomain areas and look upon these glasses as a collection of small antiferromagnetic particles. The net magnetic moment $\mu$ of the monodomains is determined by the transition ion concentration $c$ and their volume $V$, i.e., $\mu = \mu_0 \sqrt{c}\, V$, where $\mu_0$ is the magnetic moment of a single ion.$^7$ The total susceptibility of the glass consists then of contributions from all the monodomains. Since each monodomain will have its own anisotropy axis, the total susceptibility will be an average over the angle $\alpha$. Further, since we must allow for a distribution $P(V)$ of monodomain values, the total susceptibility will also be an average over volume.

In order to avoid a diverging susceptibility at $T = 0$ K, we also introduce a phenomenological exchange interaction among neighboring monodomains characterized by a paramagnetic Curie temperature. The susceptibility of the glass can then be approximated by

$$\chi_{\text{glass}} = \frac{T}{T+\Theta} \int_0^{\pi/2} d\alpha \int_0^{\infty} dV \, \chi(\alpha, V) P(V) \sin\alpha \ , \tag{7}$$

where $\chi(\alpha, V)$ is given by Eqs. (4) and (5). The only parameters of this theory are $K$, $V$, and $\Theta$. We have fitted the susceptibility of the 25.8-at.%-Co glass using two different volume distributions, namely, a Gaussian distribution and a uniform or delta-function distribution. For the Gaussian distribution the range of integration over the volume was restricted to the range of $\overline{V} \pm 3\sigma$, where $\overline{V}$ and $\sigma$ represent the average volume and standard deviation, respectively, both of which were varied in the fitting procedure. It was found that the best fit using a Gaussian distribution of volumes was obtained for a very narrow range of volumes which indicates that the monodomains are very nearly the same size, or at least the product $KV$ is uniform. With this in mind, we have fitted the susceptibility of a 25.8-at.%-Co and a 29.2-at.%-Mn glass using a uniform distribution of $K$ and $V$ values. The results are shown in Figs. 8 and 9.

The parameters required to obtain these fits were $KV/k = 20.5$, $\mu = 285\mu_B$, $\Theta = 2.0$ for the cobalt glass and $KV/k = 19.4$, $\mu = 230\mu_B$, $\Theta = 0.45$ for the manganese glass. If we take for $K \sim 10^6$ erg/cm$^3$ (which is a value typical of crystalline cobalt or

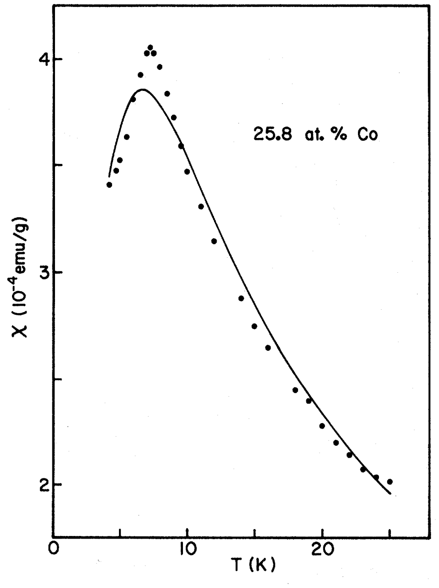

FIG. 8. Susceptibility vs temperature for a 25.8-at.%-cobalt aluminosilicate glass. Solid curve is the theoretical fit.

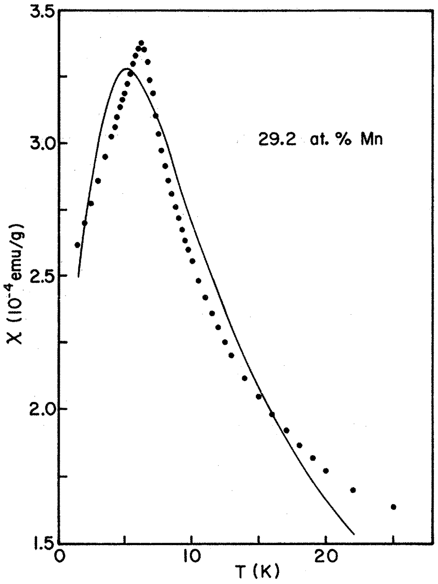

FIG. 9. Susceptibility vs temperature for a 29.2-at.%-manganese aluminosilicate glass. Solid curve is the theoretical fit.

manganese compounds), we find $V^{1/3} \sim 15$ Å. This distance does not represent the monodomain size but rather the extent of local atomic order. In order to obtain the actual size of the monodomains one must use the value for $\mu$. Utilizing the fact that $\mu = 285\mu_B \simeq 4.5\mu_B\sqrt{N}$ for the Co glass and $\mu = 230\mu_B \simeq 4.85\mu_B\sqrt{N}$ for the Mn glass, where $N$ is the number of transition metal ions in a monodomain,[7] we obtain a size of ~50 Å. This length is a measure of the extent of magnetic order in the glass. While the agreement between the theory described here and experiment is already remarkable, we can obtain even better agreement by allowing the anisotropy constant $K$ to be weakly temperature dependent. We have established that only a 10% variation of $K$ about its value at the peak temperature would yield perfect agreement with experiment. A temperature dependence of $K$ is not at all out of the question since antiferromagnetic materials usually have temperature-dependent anisotropy constants. However, we are not able to determine the precise temperature dependence of $K$ from our data since the model described here is only approximate. To obtain a further check on the model, it would be highly desirable to measure $K$ and its temperature dependence directly using suitable resonance techniques. Such a program is currently under way.[19]

Finally a work about the concentration dependence of $\chi_{\text{glass}}$. Referring to Figs. 7(a) and 7(b), it appears that the parameter $KV$ scales with the magnetic-ion concentration. This is understandable, since higher concentrations likely result in larger monodomains, leading to larger values of $KV$, and hence to broader susceptibility maxima of reduced magnitude at higher peak temperatures.

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[6] Recently, several workers have put forth similar models to account for the sharp susceptibility peaks in dilute magnetic alloys, as observed by V. Cannella, J. A. Mydosh, and J. I. Budnick [J. Appl. Phys. 42, 1689 (1971)]. Among these are J. L. Thoulence and R. Tournier (private communication) and J. A. Mydosh [Bull. Am. Phys. Soc. 19, 254 (1974)]. It should be mentioned here that such a peak in the susceptibility might alternatively indicate the existence of a spin-glass phase in which individual magnetic moments (rather than ordered groups of magnetic moments as in the monodomain model) freeze into random directions. For appropriate references see, for instance, the review articles by P. W. Anderson and B. R. Coles [*Amorphous Magnetism*, edited by H. O. Hooper and A. M. de Graaf (Plenum, New York, 1973)] and the recent article by K. Adkins and N. Rivier [J. Phys. (Paris) C 4, 237 (1974)]. In the present paper we do not attempt a critical comparison of the various models, but rather we consider to what extent a particular model is capable of accounting for the experimental observations. As we shall see, the monodomain model provides a good description of the phenomena observed in the transition-metal aluminosilicate glasses.

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[18] The anisotropy energy in crystalline materials is generally due to so-called magnetocrystalline effects. To some extent such effects will also be present in amorphous materials. However, a more important contribution to the anisotropy energy must be sought in the local strains which are invariably present in amorphous materials, as pointed out by Polk [D. E. Polk, J. Non-Cry. Solids 5, 365 (1971)]. The anisotropy constant $K$ used in this theory must be regarded as an approximate average of local anisotropy energy densities.

[19] Additional experimental evidence supporting the monodomain model can be found in the high-resolution sound-velocity measurements made by T. J. Moran, N. K. Batra, R. A. Verhelst, and A. M. de Graaf, following paper, Phys. Rev. B 11, 4436 (1975).