Amsterdam, 1970), pp. 417–433.

[2] M. D. Rechtin, J. Vander Sande, and P. M. Baldo, Scr. Met. 12, 639 (1978).

[3] J. H. Barrett, private communication.

[4] J. Neufeld and R. H. Ritchie, Phys. Rev. 98, 1632 (1955), and Phys. Rev. 99, 1125 (1955).

[5] V. N. Neelavathi, R. H. Ritchie, and W. Brandt, Phys. Rev. Lett. 33, 302 (1974).

[6] D. S. Gemmell, J. Remillieux, J.-C. Poizat, M. J. Gaillard, R. E. Holland, and Z. Vager, Phys. Rev. Lett. 34, 1420 (1975).

[7] R. H. Ritchie, private communication.

Anisotropic Spin-Glass Behavior in Fe_2TiO_5

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It is shown that the insulating oxide Fe_2TiO_5 exhibits anisotropic (uniaxial) spin-glass behavior below 55 K. Extensive experimental results supporting this conclusion, including principal magnetic susceptibility, neutron scattering, ultrasonic, specific heat, and oriented single-crystal Mössbauer measurements, are described.

We report here on a comprehensive series of investigations of the structural and magnetic properties of the insulating oxide Fe_2TiO_5. Our results lead us to conclude that this undiluted compound containing only one type of magnetic ion exhibits *anisotropic* spin-glass behavior below 55 K. We believe this to be the first observation of such behavior and, since large crystals of Fe_2TiO_5 can be readily grown, we expect that this compound will be an ideal candidate for such studies as spin dynamics and critical behavior in spin-glasses. In particular, we note that there is the possibility of studying the angular dependence of spin-glass behavior.

Fe_2TiO_5 has been reported[1] to have an orthorhombic structure (*Cmcm*) with Fe^{3+} and Ti^{4+} ions filling (8*f*) and (4*c*) sites, respectively. Powder Mössbauer spectra[2] at 4 and 50 K exhibited hyperfine splitting, with rather broad linewidths. As we succeeded in growing single crystals of this compound, we were able to carry out a series of comprehensive studies on both single-crystal and powder specimens.

In Fig. 1 we present the results of low-field principal magnetic susceptibility measurements. These were obtained with use of a magnetic susceptometer in an alternating magnetic field of 30 Oe at 1100 Hz. Other measurements, carried out in fields of 20–100 Oe at 300–2000 Hz, yielded similar results. The temperature was varied at about 3 K/min. No hysteresis or relaxation ef-

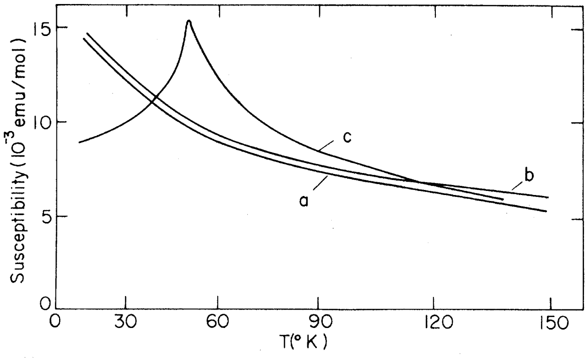

FIG. 1. Low-field principal magnetic susceptibilities parallel to *a*, *b*, and *c* crystallographic axes.

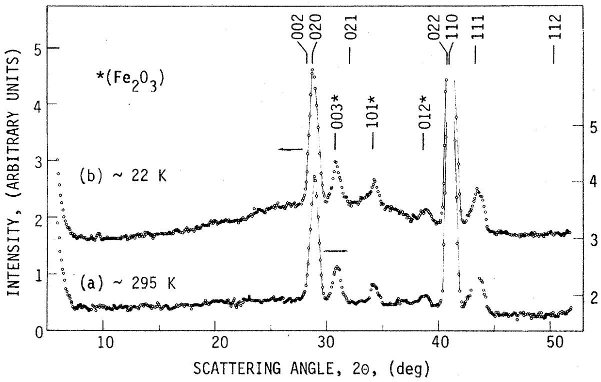

FIG. 2. Neutron diffraction scattering data recorded at (a) 295 and (b) 22 K.

fects were observed. We see from Fig. 1 that the magnetic susceptibility is strikingly anisotropic at low temperatures. The c-axis susceptibility χ_c exhibits a broad anomaly centered at $T_0 \simeq 55$ K, somewhat similar to that found in the parallel susceptibility of antiferromagnets. However, the other susceptibilities, χ_a, and χ_b, have *no* anomaly at this or any other temperature in the measured region. Both exhibit smooth, *paramagneticlike* behavior both above and below T_0. We know of no other magnetic material whose principal susceptibilities exhibit such behavior. High-field vibrating-sample magnetometer measurements (not shown), recorded in fields of 5 to 10 kOe, yielded qualitatively similar results, except that the χ_c low-field peak was significantly reduced and this susceptibility was essentially constant for $T \leq T_0$.

In an attempt to study directly the behavior of the Fe^{3+} spins in Fe_2TiO_5, powder neutron-diffraction measurements were carried out at several temperatures between 4.2 and 300 K. Some of our results are shown in Fig. 2. *No indication of long-range magnetic ordering was found.* However, analysis of the 295-K pattern showed conclusively that the Fe^{3+} and Ti^{4+} ions are essentially *randomly distributed* on the (8f) and (4c) sites, in disagreement with the reported crystallographic structure.[3] This is best established from the intensity of the {112} peak in Fig. 2. If the Fe^{3+} and Ti^{4+} ions were in crystallographically distinct sites, this reflection would have one-half the total intensity of the {002} plus {020} reflections. For random occupation, on the other hand, this peak would be essentially zero, as observed.

Since the onset of long-range magnetic ordering can also be detected by anomalies in the elastic constants,[4] we carried out ultrasonic measurements at 30 and 150 MHz for $30 < T < 80$ K. Our results are shown in Fig. 3. No anomaly is observed in the velocity longitudinal sound waves propagating parallel to the c axis. For longitudinal waves propagating perpendicular to this axis, the temperature dependence of the velocity is again essentially smooth, although there is possibly a very slight softening in the vicinity of T_0. Note that the resolution of this latter measurement is significantly higher than that of the former one, being better than 1 ppm.

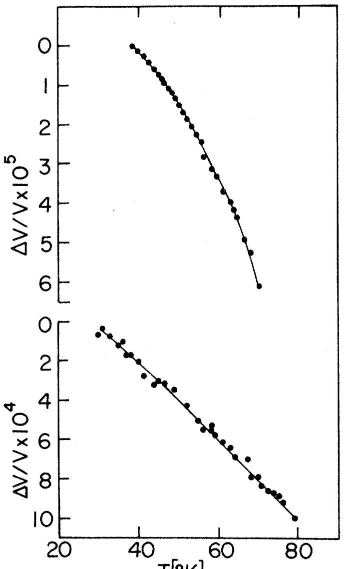

FIG. 3. Temperature dependence of the acoustic velocity for longitudinal waves propagating perpendicular (upper half, 150 MHz) and parallel (lower half, 30 MHz) to the c crystallographic axis. The lines through the data points are a guide to the eye.

We also measured the specific heat of a powder specimen of Fe_2TiO_5 for $35 < T < 80$ K, with a resolution of ± 0.1 J/mol K. No peak or other anomalous behavior was observed. Thus in neither neutron-diffraction, elastic, or specific-heat measurements do we find any evidence of long-range magnetic order in $FeTiO_5$ below 55 K.

Examples of hyperfine splitting without long-range magnetic order have been reported previously, e.g., by Kurth and Roth[5] in $CsMnFeF_6$ and by Wiedenmann[6] in $FeMgBeO_4$. However, no anisotropic behavior of the susceptibility was reported for either of these compounds. We regard this behavior as the essential new feature in our work and, in order to confirm the uniaxial dis-

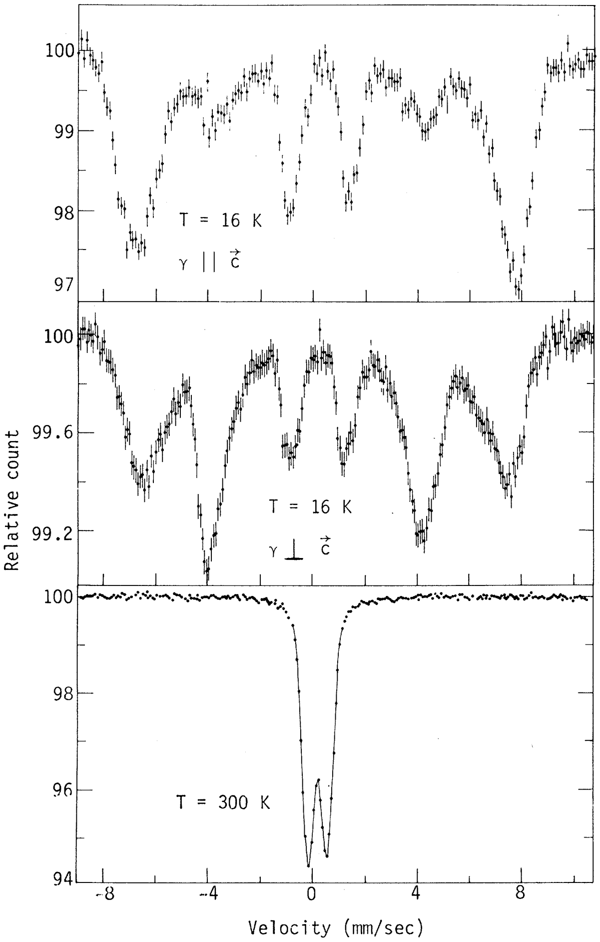

FIG. 4. Mössbauer spectra of single crystals oriented parallel and perpendicular to the c crystallographic axis.

tribution of the Fe^{3+} spins below T_0 indicated by the susceptibility data, Mössbauer studies on mosaics of *oriented* single-crystal platelets were carried out. In these experiments the crystallographic c axis was aligned either parallel or perpendicular to the direction of the γ radiation. Typical results are shown in Fig. 4. For $T > T$, we obtain a single quadrupolar-split doublet, whose isomer shift and splitting are typical of high-spin Fe^{3+}. Since the diffraction data show that Fe^{3+} ions are located on two sites which, as a consequence of the random occupation, have varying crystallographic environments, it is clear that the electric field gradient is not sensitive to this variation. For $T < T_0$, we observe hyperfine splitting with rather broad absorption lines, indicating a distribution of hyperfine fields. The main feature of these spectra, however, is that the $\Delta m = 0$ lines are markedly *suppressed* for γ radiation parallel to the c axis, while they are *dominant* when the γ radiation is perpendicular to this axis. From the selection rule associated with this transition, it immediately follows that the hyperfine fields at each site (which are coaxial with the spin orientation) are all essentially aligned with this axis. *It follows that the* Fe^{3+} *spins, for* $T < T_0$, *all lie along the crystallographic c axis, even though no long-range order exists.* No indication of any relaxation effects was observed in any of the Mössbauer spectra.

An interesting aspect of the neutron diffraction data is the presence, even at 295 K (i.e., well above T_0), of a broad diffuse background in the pattern (see Fig. 2). This is characteristic of short-range magnetic correlations and indicates that significant short-range order persists at temperatures 5 to 10 times greater than T_0. It follows that at least some of the Fe^{3+}-Fe^{3+} exchange bonds in Fe_2TiO_5 are surprisingly strong for a material exhibiting no long-range order and also explains why the effective magnetic moment μ_{eff}, as calculated from the $100 < T < 300$ K susceptibility data, is much lower than the theoretical value, $5.92\mu_B$, expected for isolated Fe^{3+} ions with $S = \frac{5}{2}$. We verified this conclusion by carrying out high-temperature susceptibility measurements, which showed that Fe_2TiO_5 exhibits true Curie-Weiss behavior (with μ_{eff} approaching the free-ion value) only at temperatures above 650 K. The paramagnetic Curie temperature extrapolated from the $650 < T < 1000$ K data is $\theta \simeq -960$ K. Thus strong antiferromagnetic bonds are clearly present. The strength of these bonds is of course substantiated by the well-developed diffuse background peak in the neutron scattering data, Fig. 2. This peak increases in intensity with decreasing temperature down to about 40 K, below which it is essentially temperature independent. Only at high temperatures ($T \gtrsim 650$ K) do the short-range correlations responsible for non-Curie-Weiss behavior and the diffuse peak disappear.

All our data are consistent with the conclusion that Fe_2TiO_5, below $T_f \equiv T_0 \simeq 55$ K, is in an anisotropic spin-glass state. As our high-temperature susceptibility results show that the dominant interaction mechanism in this compound is antiferromagnetic exchange, the question arises as to why Fe_2TiO_5 freezes into such a state instead of ordering antiferromagnetically. For the case of dilute alloys, it is believed that spin-glass behavior is a consequence of competition between ferromagnetic and antiferromagnetic interactions.[7]

In fact, it is precisely such a competition which underlies the well-known Edwards-Anderson model[8] of the spin-glass state. However, the more or less balanced positive and negative interactions intrinsic to this model are not likely to be found in magnetic insulators. Thus it is much more probable that frustration[7] rather than competing interactions is the essential key to understanding why a spin-glass phase occurs in Fe_2TiO_5.

An examination of the unit cell and atomic site parameters of Fe_2TiO_5 reveals that the $(8f)$ and $(4c)$ sites form an array of interconnected triangles. As the very strong antiferromagnetic interactions in Fe_2TiO_5 are certainly due to short-range exchange, it is clear that the random occupation of $\frac{1}{3}$ of there sites by nonmagnetic ions results in these exchange interactions having a random aspect. Recently Villain[9] has shown how various models for insulating magnetic materials having random features can be transformed into the Edwards-Anderson model, even when the interactions are predominantly or even all antiferromagnetic. However, Fe_2TiO_5 does not seem to be described by any of these models. In particular, this material does not appear to be quasi one dimensional, but rather two dimensional, with interlocking sets of zig-zag chains along the a and c axis. Thus, although we have been able to obtain, with a modified Edwards-Anderson model, theoretical susceptibilities that are in qualitative agreement with our experimental data, it is clear that further analysis will be required to understand the mechanisms responsible for the anisotropic spin-glass behavior of Fe_2TiO_5.

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[1] R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1964), Vol. 3, p. 297.

[2] S. Muranaka, T. Shinjo, Y. Bando, and T. Takada, J. Phys. Soc. Jpn. 30, 890 (1971).

[3] We recently learned that a similar conclusion was reached by M. G. Miksic, M. D. Miller, and D. E. Cox, in Proceedings of the International Conference on Magnetic Orders, Bucharest, 1968 (unpublished).

[4] See, e.g., C. W. Garland, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thruston (Academic, New York, 1970), p. 51.

[5] W. Kurtz and S. Roth, Physica (Utrecht) 86-88B, 715 (1977).

[6] A. Wiedenmann and P. Burlet, J. Phys. (Paris) Colloq. 39, C6-720 (1978).

[7] For a review, see A. Blandin, J. Phys. (Paris) Colloq. 39, C6-1499 (1978).

[8] S. F. Edwards and P. W. Anderson, J. Phys. F 5, 965 (1975).

[9] J. Villain, Z. Phys. B33, 31 (1979).

Electron Tunneling Spectroscopy of High-Speed W-Ni Submicron Junctions

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It is shown that electron tunneling in mechanically contacted high-speed submicron junction occurs in the presence of tens of kilobars of local stress. The observations are made under highly controlled conditions. Sharp tunneling resonances originating from a band-structure effect related to Ni ferromagnetism are observed and their stress and magnetic shifts studied.

High-speed metal-oxide-metal junctions of the type employed in harmonic-frequency mixing and frequency measurements in the infrared[1,2] form a class of electron tunneling junctions with novel physical properties. The high-speed performance requires a low junction capacitance. This in turn dictates a small junction area—our high-speed junctions have measured dimensions in the submicron range. Such junctions differ in several important respects from the tunneling junctions previously studied. These differences are as follows:

(a) The potential barrier in a low-impedance (below several hundred ohms) submicron junction is very thin (less than 7 or 8 Å thick).

(b) An abnormal barrier having a very low barrier height as well as a low barrier thickness can become detectable and cause a readily measurable tens-of-ohms impedance in a submicron junction. The same barrier in a large-area junction