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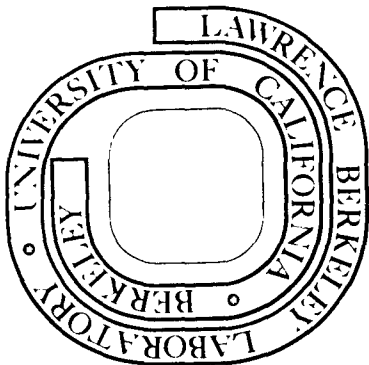Richard C. Wilson and Rollie J. Myers

October 1975

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Electron Paramagnetic Resonance Spectrum and Spin Relaxation for

$Ti(H_2O)_6^{3+}$ in Aqueous Solution and in Frozen Glass

by

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ABSTRACT

The EPR spectra of acidified solutions of Ti(III) were observed both above and below the freezing point. In the frozen glass, an axial spin Hamiltonian was found for the $Ti(H_2O)_6^{3+}$ complex with $g_{\parallel} = 1.988 \pm .002$ and $g_{\perp} = 1.892 \pm .002$. When warmed above $-50°C$, broadening occurs which follows $\frac{1}{T_2} = 2.90 \times 10^{14} e^{-\Delta E/kT}$ sec^{-1}, where $\Delta E = 1850 \pm 50$ cm^{-1}. This same broadening is followed for both the solution and frozen glass. The g-values are explained assuming that the 1850 cm^{-1} value is the first excited orbital state energy, and the relaxation is explained as a resonant Raman process.

Introduction

Titanium (III) has a single unpaired electron in a 3d orbital giving a ^2D state for the free ion. A crystal field of octahedral symmetry will split this five-fold degenerate state into an orbital doublet, ^2E_g, and an orbital triplet, $^2T_{2g}$, with the triplet lower in energy. Under these circumstances the g-values for the ground state and its spin relaxation depend a great deal upon the interplay of the orbital angular momentum, the spin-orbit interaction and any deviations from octahedral symmetry.

In a very early theoretical paper, Van Vleck[1] showed that both direct spin-phonon and Raman processes should be important for the low temperature spin relaxation of $Ti(H_2O)_6^{3+}$ in crystals with the expected amount of distortion along a trigonal axis. Experimental work on Ti^{3+} in Al_2O_3[2] and on $Ti(H_2O)_6^{3+}$ in crystals such as $CsTi(SO_4)_2 \cdot 12H_2O$[3] indicated quite large orbital contributions to the g-values and very fast spin relaxation above 50 K.

Our major interest was in Ti^{3+} in aqueous solution where the most important species should be $Ti(H_2O)_6^{3+}$. Charles[4] reported that a broad electron paramagnetic resonance spectrum could be observed at room temperature for acidified solutions of Ti^{3+}. We first checked these results[5] and then discovered[6] a nice sharp spectrum for frozen glasses of our aqueous solutions. We also observed, however, that when we warmed our glasses above 100 K, a broadening occurs which continues right through the melting point of the solution. Recently, other reports have appeared[7,8] which give g-values for a frozen glass similar to ours. This paper reports on both our glass spectrum and on the spin relaxation that we have observed for $Ti(H_2O)_6^{3+}$.

Experimental Methods

Titanium (III) was obtained from Alfa Inorganic in the form $TiCl_3$ and from Sargent Chemical Company in a 1 M solution of $Ti_2(SO_4)_3$. The concentrations of the titanium in the samples used varied from 0.5 M to 3 M. Comparison of the data obtained at high Ti(III) concentrations with that for low concentrations showed negligible effects from Ti-Ti interactions. All samples were approximately 1 M in acid to prevent hydrolysis to $Ti(H_2O)_5OH^{2+}$. In all cases a nitrogen atmosphere was used to minimize oxidation of the titanous ion.

The samples were usually contained in a Varian E-248-1 aqueous solution sample cell. K-band (24 GHz) spectra were obtained with the sample sealed in a quartz tube.

X-band (9 GHz) measurements were carried out on a Varian V-4502 EPR spectrometer equipped with a 9-inch magnet, and a Fieldial coupled to an X-Y recorder. The temperature was controlled by a Varian V-4540 variable temperature controller connected to a Varian V-4557 variable temperature accessory. The modulation frequency was 100 kHz. The cavity was a Varian V-4531 multipurpose rectangular cavity.

S-band (3 GHz) measurements were carried out on a spectrometer constructed in this laboratory, which utilizes a wave guide circulator. The S-band cavity was designed by James Chang and the modulation frequency was 100 kHz.

K-band measurements were carried out on a bridge of similar design also constructed in this laboratory. The cavity was fabricated from brass rectangular waveguide and silver plated. The cavity was contained in a double dewar system and maintained at 77 K. The modulation frequency was 800 Hz.

Field measurements were made using an NMR gaussmeter with the proton resonance frequency measured by a frequency counter. The frequency counter was also used to measure the klystron frequency.

The temperature was measured using a copper-constantan thermocouple in the gas stream immediately above the middle of the cavity. The thermocouple was calibrated at 77 K and at 373 K. The precision of the temperatures obtained was thought to be ±0.5°.

Experimental Results

The spectrum shown in Fig. 1 is that of a rapidly frozen solution of $TiCl_3$ in 1 M H_2SO_4. This spectrum can be readily assigned to randomly oriented spins with an axial spin Hamiltonian, and even at K-band there is no evidence of symmetry less than axial. These spectra are rather well fit by computer simulations and the g-values obtained are $g_{||} = 1.988\pm0.002$ and $g_\perp = 1.892\pm0.002$. Our values agree well with Glebov[7] for $TiCl_3$ in HCl where he reported $g_{||} = 1.98$ and $g_\perp = 1.89$. There is, however, noticeable disagreement with Premovic and West[8] who report $g_{||} = 1.994\pm0.001$ and $g_\perp = 1.896\pm0.001$. It seems apparent that they were not using computer simulations to fit their spectra and as Ibers and Swalen[9] observed, very narrow crystallite linewidths must be present before reliable magnetic parameters can be obtained from the position of the maximum and the inflection point of an absorption spectrum.

We also prepared glass spectra using HCl and HSO_3CF_3 as acids. Like Premovic and West[8], we found no evidence that the anion affected the g-values. Some glasses, however, did give narrower crystallite linewidths which resulted in better resolution and more intense spectra with a derivative presentation.

When the glass spectra were warmed to dry ice temperatures, a broadening is observed and the spectrum approaches a symmetrical Lorentzian at -40°C and up through the melting point a broad symmetric absorption can be observed if sufficient modulation amplitude is utilized. This broad line shows no change in shape or width when the glass melts and at room temperature one observes the same spectrum as reported by Charles.[4]

Figure 2 shows how the peak-to-peak splitting (ΔH) in the first derivative spectrum for the frozen glass and the solution varies with temperature. It is clear from these data that the relaxation follows the form

$$\frac{1}{T_2} = \frac{\gamma \Delta H \sqrt{3}}{2} = A\, e^{-\Delta E/kT} \qquad , \qquad (1)$$

where γ is the appropriate magnetogyric ratio. A least squares analysis of the data shown in Fig. 2 gives an activation energy $\Delta E = 1850 \pm 50$ cm^{-1} and a pre-exponential factor $A = 2.90 \times 10^{14}$ sec^{-1}. The same broadening was observed for frozen glasses and solutions containing different anions. We also observed the same broadening at S-band as we did at X-band.

The fact that this broadening follows an exponential form means that it must be due to a resonant Raman process of the type discussed by Orbach.[10] It is not unexpected that Ti^{3+} should have this means of spin relaxation at higher temperatures, since the necessary orbital states should be present. For Ti^{3+} in Al$_2$O$_3$, such a relaxation is observed,[11] but much lower lying states are involved. The remarkable thing about our observations for Ti(H$_2$O)$_6{}^{3+}$ is that such a large activation energy can be observed and that the same rate is observed for both solids and liquids. Measurements were also made using D$_2$O instead of H$_2$O as a solvent and the same broadening was observed.

While we are only able to measure the width of the EPR signal and to deduce a T_2 value, this can also be interpreted as a T_1 value. In resonant Raman relaxation one has the circumstance that $T_1 = T_2$.

Discussion

If the observed spin relaxation is due to a resonant Raman process, the 1850 cm^{-1} ΔE value should represent an excited orbital state energy for the $Ti(H_2O)_6^{3+}$. That the orbital states are so high in energy is in agreement with the fact that the g-values are so close to 2.0. For Ti^{3+} in Al_2O_3, $g_{||} \sim 1.0$ and $g_{\perp} \sim 0$. At the same time $\Delta E \sim 30$ cm^{-1}, so that large orbital contributions to the g-values are obtained when ΔE is close to λ, the spin-orbit constant.

g-values. - The application of simple crystal field equations to the g-values of $Ti(H_2O)_6^{3+}$ in single crystals has only had limited success.[12] However, we are in agreement with Premovic and West[8] that the closeness of $g_{||}$ to the free electron value can only be explained by a trigonally distorted octahedron or D_{3d} symmetry. For titanium (III) acetylacetonate in the Al(III) lattice, McGarvey[13] found $g_{||} = 2.000\pm0.002$ and $g_{\perp} = 1.921\pm0.001$. In this case, crystal structure work has established a site of D_3 symmetry. These g-values for Ti^{3+} in a chelate are similar to what we find for $Ti(H_2O)_6^{3+}$. In the chelate, however, both g-values are even closer to the free electron value.

McGarvey presents equation for the g-values which are an extension of the work of Ray[14] and include the effects of covalent bonding on the second order terms. McGarvey's equations are:

$$g_{||} = 2.0023 - 2(2.0023 + \kappa_{\pi\pi})\cos^2\alpha + \frac{4\lambda\kappa_{\pi\pi}\kappa_{\sigma\sigma}(\cos^2\alpha + \sqrt{2}\sin\alpha\cos\alpha)}{E_b - A_1} \quad , \tag{2}$$

$$g_{\perp} = 2.0023 - 2.0023\cos^2\alpha - 2\sqrt{2}\,\kappa_{\pi\pi}\sin\alpha\cos\alpha$$
$$- \frac{2\lambda\kappa_{\pi\pi}\kappa_{\sigma\sigma}(2\sin^2\alpha + \sqrt{2}\sin\alpha\cos\alpha)}{E_b - A_1} \quad , \tag{3}$$

$$\tan\alpha = [(\Delta - \lambda_1/2) + (\Delta^2 + \lambda_1\Delta + 9\lambda_1^2/4)^{\frac{1}{2}}]/\sqrt{2}\,\lambda_1 \quad , \tag{4}$$

and
$$\lambda_1 = \kappa_{\pi\pi}\lambda \quad , \tag{5}$$

where λ is the free ion spin-orbit coupling constant, Δ is the splitting from the ground state to the first excited state, $E_b - A_1$ is the octahedral field splitting, and $\kappa_{\pi\pi}$ and $\kappa_{\sigma\sigma}$ are the covalent bonding parameters for π-type bonding and σ-type bonding, respectively. Equations (2-4) assume that the dominant crystal field is the octahedral field and that the trigonal field splits the T_{2g} level into a singlet A_1 level and a doublet E_a level with the singlet being the ground state.

McGarvey's results indicate that the lowest excited orbital state energy in the acetylacetonate is $3\pm1 \times 10^3$ cm^{-1}. The slightly lower g-values in $Ti(H_2O)_6^{3+}$ would be expected to shift this value toward 1.85×10^3 cm^{-1}.

The 1850 cm^{-1} energy is expected to be close to $\Delta + \frac{1}{2}\lambda$. Substituting this approximation into Eq.(5) and setting $\lambda = 154$ cm^{-1}, our g-values can be fit using Eqs.(2-4). The two g-values are not very sensitive functions of the σ-orbital parameter, but to obtain an exact fit to the observed g-values within the limits of their errors we find that $\kappa_{\pi\pi} = 0.96\pm0.12$ and $\kappa_{\sigma\sigma} = 1\pm0.7$. These values are reasonable when compared to the much larger amounts of covalency which are often used to explain transition metal complexes.

We can conclude from these results that the g-values that we observe for $Ti(H_2O)_6^{3+}$ are completely consistent with a complex of D_{3d} symmetry with an excited orbital state at the same energy as indicated by the resonant Raman relaxation.

Jahn-Teller distortion. - The most surprising aspect of the ΔE value is that it is so large. Simple generalizations about t_{2g} electrons being non-bonding led Ballhausen[15] to expect small Jahn-Teller splittings in the $^2T_{2g}$ term. However, the calculations of Van Vleck[16] indicate that $Ti(H_2O)_6^{3+}$ should have a trigonal distortion (D_{3d}) and Van Vleck's final value[17] for this splitting (1000 cm^{-1}) is reasonably close to our value. Most calculations of Jahn-Teller splittings have difficulty agreeing with experiment, and the agreement in this case must be only taken as confirmation of the weakness of the simple bonding reasoning.

In addition to these theories one does find that in $CsTi(SO_4)_2 \cdot 12H_2O$ that the $Ti(H_2O)_6^{3+}$ units are trigonally distorted.[18] In this case, however, the g-values of the Ti^{3+} are rather close to 1.0, not close to 2.0 as we find for the complex in a frozen glass. Recent evidence[19] indicates that in $CsTi(SO_4)_2 \cdot 12H_2O$ there is a dynamic Jahn-Teller distortion. In the frozen glass the large orbital splitting would indicate a static Jahn-Teller distortion. In the $CsTi(SO_4)_2 \cdot 12H_2O$ the full Jahn-Teller distortion that we observe must be restricted by its lattice.

The room temperature line width is 2400 ± 200 gauss and this limits the accuracy of the solution g-value measurements, but they are consistent with the $g_{\parallel}$ and $g_{\perp}$ we find for the frozen glasses. Accurate magnetic suscepti- bilities do not appear to have been measured for acidified solution of Ti^{3+}.

While the evidence is limited, it seems almost conclusive that the g-value for frozen glasses of Ti^{3+} correspond to the $Ti(H_2O)_6^{3+}$ complex without additional lattice effects.

From the visible absorption spectra of Ti^{3+} in solution it has been estimated[20] that the Jahn-Teller splitting in the ^2E_g state is also about 2000 cm^{-1}. In addition to poor resolution, one has the complication that the ^2E_g term is only split by a tetragonal distortion while the $^2T_{2g}$ ground term is surely trigonally distorted. Since the ^2E_g term in $Cu(H_2O)_6^{2+}$ has Jahn-Teller splittings of this magnitude, we are forced to conclude, as all the available evidence suggests, that the Jahn-Teller splittings for both the lower and upper crystal field terms are of similar magnitudes, despite the different bonding available to $t2g$ and eg electrons.

Spin relaxation. - In the previous sections we saw that the 1850 cm^{-1} energy is consistent with the g-values of a trigonally distorted complex. This serves to explain the ΔE value in Eq.(1), but it remains to account for the A value. While there is some variation to the pre-exponential factor in resonant Raman relaxation, this variation seems to follow a theoretical pattern.

An examination of the experimental A values[21] for various ions reveals that for many Lanthanide ions $A \approx 10^9$ sec^{-1} with $\Delta E \approx 30$ cm^{-1} and for a few of the Transition-metal ions $A \approx 10^{11}$ sec^{-1} with $\Delta E \approx 200$ cm^{-1}. This clear increase in A with ΔE is explained by the usual formulation[10] for resonant Raman relaxation. Abragam and Bleaney[22] have approximated $1/T_1$ for a number of Lanthanide ions with resonant Raman relaxation as

$$\frac{1}{T_1} \sim 10^4 \Delta^3 e^{-\Delta/T} \qquad , \qquad (6)$$

where Δ is ΔE in units of degrees. If we apply this approximate relation to $Ti(H_2O)_6^{3+}$ with $\Delta E = 1850$ cm^{-1}, it predicts that $A \sim 2 \times 10^{14}$ sec^{-1}. This is very close to the value that we find.

Another approach would be to use the electric-field fluctuation equations derived by Kivelson[23] for Orbach or resonant Raman relaxation in liquids. Since we find no change in relaxation upon melting of the glass, it would seem that the fluid nature of the medium plays no role in the relaxation. Kivelson's equation for Orbach relaxation assumes that a non-fluid lattice would give no relaxation. In addition, his equation cannot predict appreciable contributions to the broadening when $\Delta E/hT \sim 10$. We are forced to the conclusion that the only phonons that are important in the resonant Raman relaxation of $Ti(H_2O)_6^{3+}$ are those that are associated with molecular vibrations of the complex.

A study of the aqueous solutions of various chelates of Ti(III) by Watanabe and Fukiwara[24] has also shown large changes in line width at higher temperatures. As we observe, these were field independent and they assumed an Orbach mechanism. They did, however, try to fit this broadening to Kivelson's equation. It would seem more reasonable that this relaxation would also be observed in solids and the fluidity of the solvent would not be expected to play a real role. McGarvey[13] appeared to observe this kind of broadening in his single crystal work on the acetylactonate of Ti(III).

Acknowledgment:

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Figure Captions

Fig. 1.   The experimental spectra at 24 GHz for $TiCl_3$ in 1 M H_2SO_4 at 77 K.
The indicated positions for the g-values are based upon computer
simulations.

Fig. 2.   First derivative line width ΔH for $Ti(H_2O)_6^{3+}$ in frozen glass and
in solution.   The values for ΔH greater than 1,000 G are for
liquid solutions.   Note that there is no discontinuity in ΔH
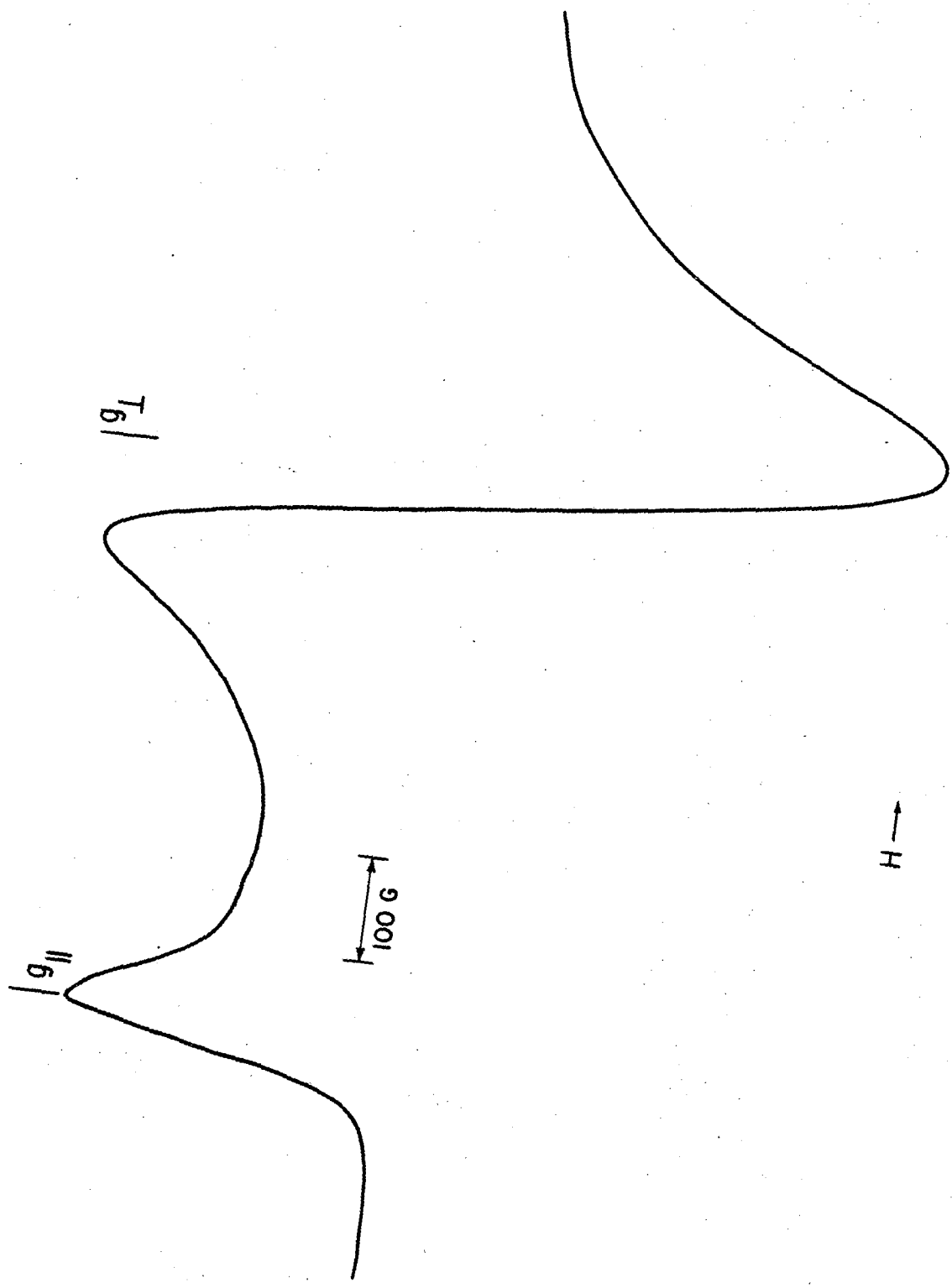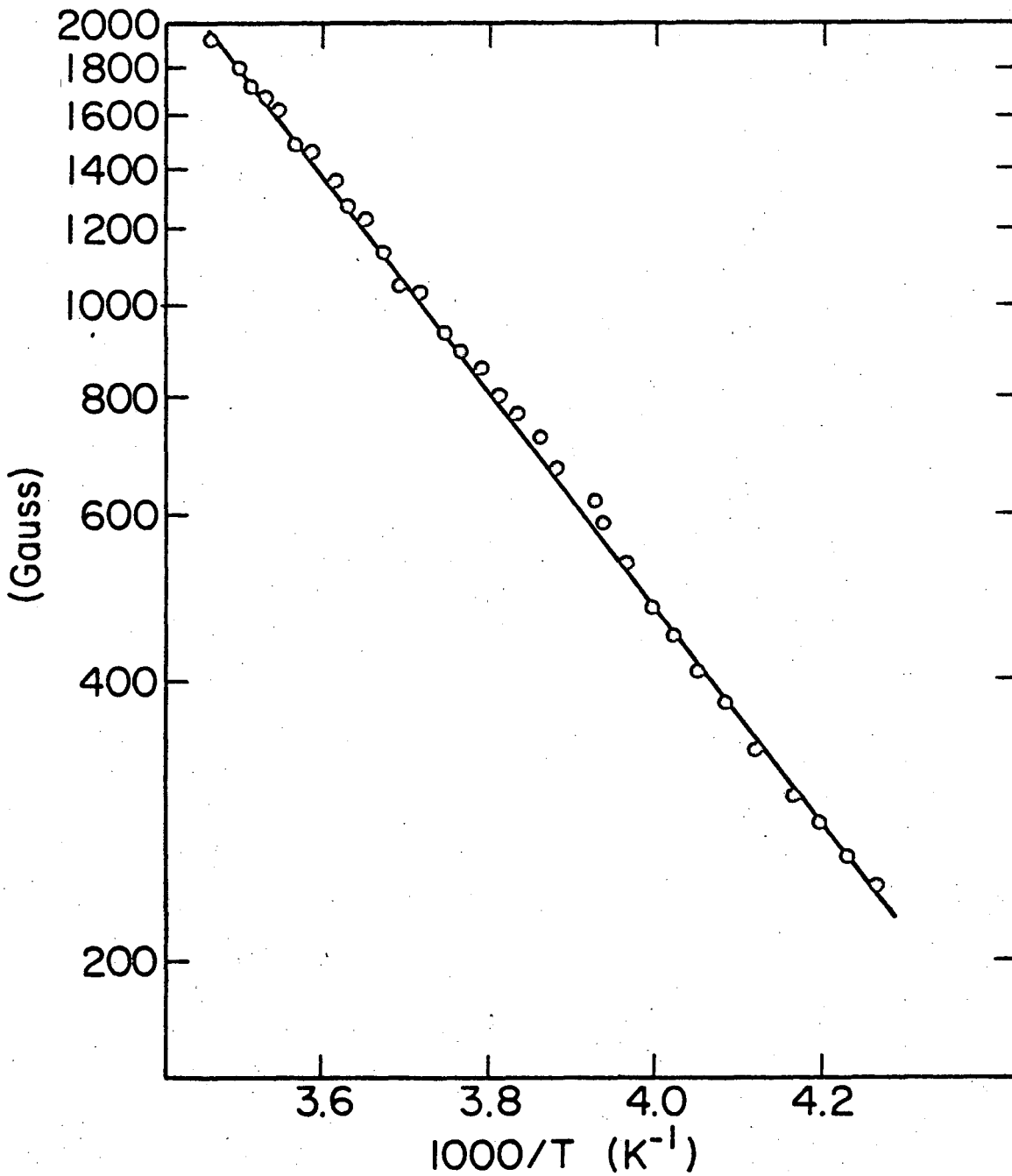upon melting.

Figure 1

$|g_\perp$

$|g_\parallel$

100 G

H →

XBL 759-7181

Figure 2

XBL 759-7172