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375 GHz EPR Measurements on Undiluted Cr(V) Salts. The Role of Exchange Effects and *g*-Strain Broadening in Determining Resolution in High-Field EPR Spectroscopy of $S = \frac{1}{2}$ Paramagnets

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This Communication reports on our recent variable-frequency (100–375 GHz) EPR measurements on several Cr(V)-containing paramagnetic compounds in their neat, undiluted form. This study was undertaken with the view of examining the role of *g*-strain (*1–4*) and exchange effects in the broadening of signals in EPR spectroscopy at Zeeman fields much higher than those being currently utilized in most laboratories.

Earlier examples of utilization of high frequencies for accomplishing higher dispersion of the *g*-tensor components are numerous. These studies include measurements at 95 GHz by Wang *et al.* (*5*), Prisner *et al.* (*6*), Burghaus *et al.* (*7*), and Smirnov *et al.* (*8*); at 145 GHz by Lebedev and co-workers (*9*), and Gerfin *et al.* (*10, 11*); at 250 GHz by Freed and co-workers (*12, 13*); and at even higher frequencies by Un *et al.* (*14*). These studies focused on systems that contained free radicals in millimolar or smaller concentrations where spin-exchange effects are small. The present work focuses on the resolution of the *g* tensor for pure compounds, wherein spin-exchange effects are important and the materials in fact undergo paramagnetic–antiferromagnetic phase transitions. The present work clearly suggests that at least for the $3d^1$, $S = \frac{1}{2}$ systems studied here, the EPR spectral resolution improves remarkably with the increase in the Zeeman field in the range investigated, up to about 14 T.

The Cr(V) compounds investigated were the alkali-metal peroxychromates, such as K_3CrO_8, Na_3CrO_8, and their mixed salt K_2NaCrO_8, in which the unpaired electron occupies the 3*d* atomic orbital on Cr. These compounds are easily synthesized by the reaction of H_2O_2 and the corresponding chromate in alkaline solutions as described elsewhere (*15–18*). These compounds were selected because (a) they are ideal for examining processes related to the *g* tensor because they exhibit very simple EPR spectra when used as powders, the resonance due to the electron Zeeman (*g*-tensor) interaction only, without any hyperfine or quadrupole effects; (b) these compounds have the simplest electronic structure for transition metals, one unpaired electron in a 3*d* orbital; (c) their crystal structure is simple, exhibiting either tetragonal or orthorhombic symmetry with 2–4 molecules per unit cell (*18–20*); and (d) they have been well characterized by magnetic susceptibility as well as EPR spectroscopy at the conventional fields (0.35 T, 9.5 GHz) (*15–18*). However, the earlier (low-field) data led to inconclusive results regarding even such basic parameters as the symmetry of the ground state, i.e., whether it was $d_{x^2-y^2}$ or d_{z^2} (*15–18*). The much superior spectral data obtained in this study suggests that the lack of resolution in the earlier EPR spectra was the result of a combined effect of electronic spin exchange, the *g* strain, and the small Zeeman splitting possible at the (low) fields employed.

All EPR spectra presented here were obtained using the high-field electron magnetic resonance facility at the National High Magnetic Field Laboratory in Tallahassee, Florida. The EPR spectrometer design is similar to that described earlier by Mueller *et al.* (*21*) with the following modifications. The source of the millimeter wave radiation is a Gunn oscillator (AB Millimetre, Paris). This source is tunable over the range 92–98 GHz, and is equipped with a set of Schottky-diode harmonic generators and filters which enable it to operate also at frequencies around 190, 285, and 380 GHz. The frequency was measured by an EIP580 counter which also served as a phase lock source for the Gunn oscillator. The Zeeman field is provided by an Oxford Instruments Teslatron superconducting magnet that is capable of field

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sweeps from 0 to 17 T. The resonance absorption is measured at a fixed frequency by monitoring the transmitted power as a function of the applied magnetic field that is swept through the resonance in either increasing or decreasing mode. A liquid helium-cooled hot-electron InSb bolometer from QMC (London, England) is used as the power detector.

As usual for EPR, the spectra are recorded in the first derivative mode, using magnetic field modulation at audio frequencies (2–10 kHz). The sample temperature can be controlled over the range of 1.4–300 K using an Oxford Instruments CF-1200 continuous-flow helium cryostat. The *g* factors were obtained by simultaneously recording the EPR spectrum of the peroxychromates and a reference powder sample of Mn^{2+} (0.1% in MgO) at frequencies around 190 GHz, following the procedure of Burghaus *et al.* (*22*).

Figures 1–3 show typical powder EPR spectra obtained at various millimeter-wave frequencies (bottom), together with the corresponding spectra taken at the commonly used (X-band) frequencies (top). The spectra result from the Zeeman interaction of the $3d^1$ unpaired electron on ^{52}Cr (nuclear spin $I = 0$), which is the main isotope of Cr (*15–18*). Thus, there is no hyperfine interaction expected, and the spectra should reflect peaks at the principal values of the *g* tensor for each compound. For a lattice with tetragonal symmetry, we thus expect the spectra to exhibit only two peaks in the first-derivative presentation: one corresponding to the resonance absorption of molecules whose tetragonal axis is oriented along the Zeeman field (labeled $g_\parallel$), and the other absorption from those molecules whose tetragonal axis is aligned perpendicular to the field direction (labeled $g_\perp$).

Figure 1 serves to illustrate this case. Here the sample is K_3CrO_8, which is known to possess tetragonal symmetry (*19*). As may be noticed from the spectrum at the top of Fig. 1, even at the low field of 0.35 T, there are indications of two peaks. As discussed in the earlier studies (*15–18*), the lack of resolution in this spectrum results partly from spin-exchange effects and partly from the *g*-strain broadening processes. Of course, the spin-exchange frequency has little or no dependence on the Zeeman field while the *g* strain is expected to be proportional to the field, although the exact, quantitative form of this field dependence is hard to predict. The evidence for the existence of exchange and dipolar effects was that the signal linewidths were found to become narrower by an order of magnitude on diluting K_3CrO_8 in its diamagnetic host K_3NbO_8 (*15, 23*). It was thus of critical importance to examine whether the EPR spectral resolution improves with the increase in the Zeeman field in this simple model case. The spectrum at the bottom of Fig. 1 shows the effect of increasing the Zeeman field to about 10 T: at this field, the presence of two peaks becomes clearly evident. The two peaks are marked $g_\parallel$ and $g_\perp$ as usual, and the measured values are $g_\parallel = 1.9431$ and $g_\perp = 1.9852$, which are consistent with the *g*-tensor values of K_3CrO_8 diluted in a niobate matrix (*15, 23*). This result suggested that the *g* strain may not be a significant deterrent to the expected enhancement in spectral resolution at high fields.

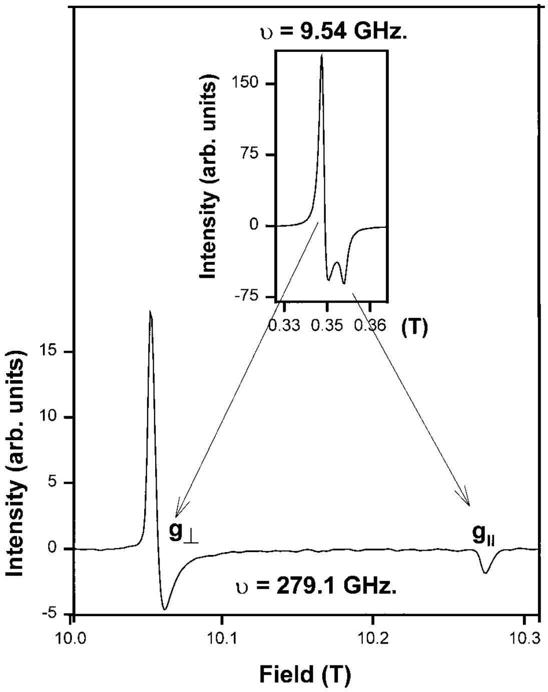

FIG. 1. EPR spectra of K_3CrO_8 powder taken at 9.54 GHz (top) and 279.1 GHz (bottom). Note the superior resolution of the $g_\parallel$ and $g_\perp$ peaks in the 279.1 GHz spectrum.

Encouraged by this observation, we measured the corresponding spectra for the cases of lower-symmetry lattices of K_2NaCrO_8 and Na_3CrO_8, which would be expected to exhibit an additional, third peak. The X-band EPR spectrum for K_2NaCrO_8 (Fig. 2, top) has a shoulder, but no indication of a third peak. This low-field shoulder merely implies that $g_\parallel > g_\perp$, while the K_3CrO_8 spectra (Fig. 1, both upper and lower) are clearly a case of $g_\perp > g_\parallel$ in both low and high field. In the case of K_2NaCrO_8, the enhancement in resolution was essential for any further understanding of the spectral details.

The spectrum shown in the lower part of Fig. 2, taken at the Larmor frequency of 287.2 GHz and field around 10.5 T, demonstrates the significant resolution enhancement over that at the low field (top): the high-field spectrum consists of three well-resolved peaks, labeled by their *g*-tensor components, $g_x = 1.9636$, $g_y = 1.9696$, and $g_z = 1.9851$. It is also now evident that $g_z > g_{x,y}$, thus confirming the indication for this result from the low-field spectra. The conclusion that the electronic ground state wavefunction for K_2NaCrO_8 is d_{z^2} versus $d_{x^2-y^2}$ for K_3CrO_8 is indeed intriguing.

As a more stringent test for resolution enhancement, we measured the EPR spectra for Na_3CrO_8 at both low field (0.35 T) and high field (around 13.5 T). The results are shown in Fig. 3. The low-field spectrum in Fig. 3 shows just a single peak while three were expected. However, the spectrum started to develop new features as the Larmor frequency was raised above 190 GHz, and a well-resolved spectrum was detected at 374.6 GHz (Fig. 3, lower spectrum). The three peaks here correspond to $g_x = 1.9848$, $g_y = 1.9802$, and $g_z = 1.9544$. It may be noted that these values reflect the ground state to be $d_{x^2-y^2}$, the same as that for K_3CrO_8 (Fig. 1), but in contrast to the case of d_{z^2} for K_2NaCrO_8 (Fig. 2). The example of Na_3CrO_8 clearly demonstrates that high-field EPR measurements can yield not just quantitatively but qualitatively new information on the point symmetry and electronic properties of paramagnetic systems.

In conclusion, this study establishes the following. First, the broadening of EPR peaks due to *g* strain and any related phenomena does not seem to adversely affect the spectral resolution in high-field EPR measurements of $S = \frac{1}{2}$ systems such as those investigated here. Second, the resolution enhancement becomes better with higher applied Zeeman fields up to the strengths of 14 T, the highest value used in this study. Third, the resolution enhancement is very significant in that a single unresolved peak at the conventional fields (<1 T) can split into its three *g*-tensor components at 10 T and above. Earlier, to overcome the broadening effects due to dipolar and exchange interaction, one had to dilute the paramagnetic ions in a diamagnetic host [e.g., diluting K_3CrO_8 in its diamagnetic host K_3NbO_8 (*15, 23*)]. Such high-field spectra as obtained in this study can thus yield qualitatively new information on the point symmetry and electronic wave functions of at least simple $S = \frac{1}{2}$ paramagnets, without any recourse to dilution. An important observation is that the linewidths are about the same at X-band (9.45 GHz) as at 375 GHz. Extension of this work to other $S > \frac{1}{2}$ systems, and temperature and field dependence of the resolution-enhancement process and its relationship to electron-spin-exchange processes is currently in progress.

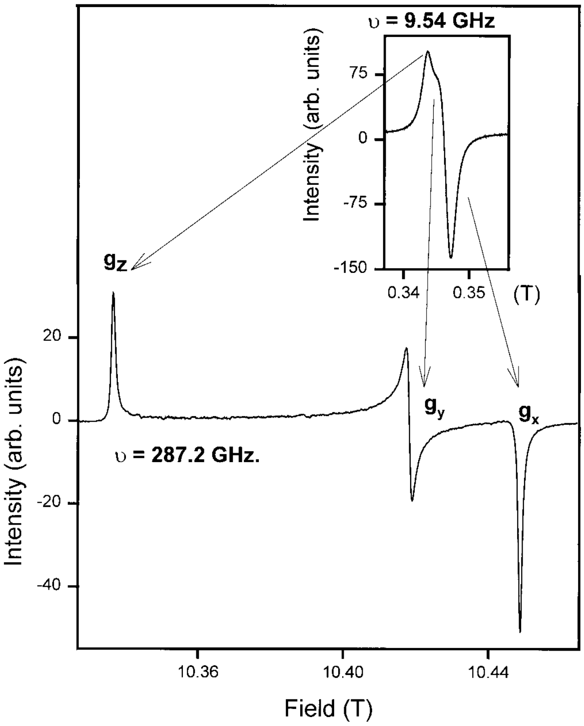

FIG. 2. EPR spectra of K_2NaCrO_8 powder measured at 9.54 GHz (top) and at 287.2 GHz (bottom). Notice the unresolved doublet (top) is split into a distinct triplet at high field (bottom).

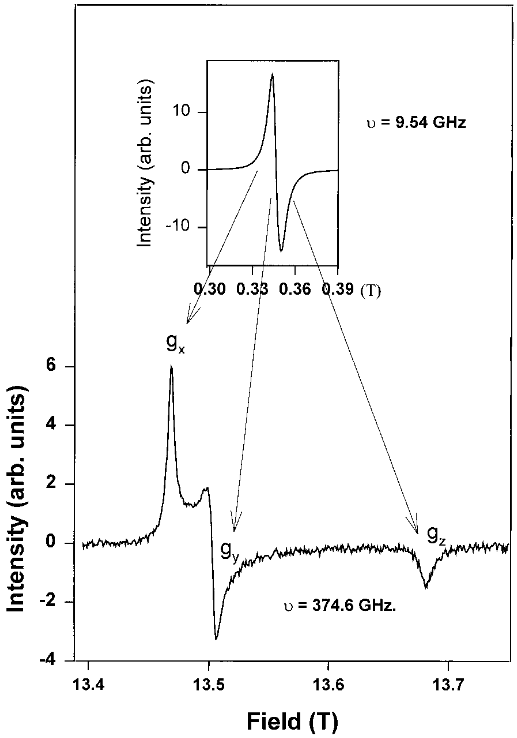

FIG. 3. Comparison of the EPR spectra of Na_3CrO_8 powder at low and high frequencies. The upper spectrum was taken at 9.54 GHz, while the lower spectrum was measured at 374.6 GHz. Notice how the singlet (top) has been split into three peaks (bottom), representing the three principal components of the *g* tensor.

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