Electronic spin resonance and exchange paths in the orthorhombic dimer system Sr$_2$VO$_4$

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We report on susceptibility and electron spin resonance (ESR) measurements at X- and Q-band frequencies of Sr$_2$VO$_4$ with orthorhombic symmetry. In this dimer system, the V$^{4+}$ ions are in tetrahedral environment and are coupled by an antiferromagnetic intradimer exchange constant $J/k_B \approx 100$ K to form a singlet ground state without any phase transitions between room temperature and 2 K. Based on an extended Hückel tight-binding analysis, we identify the strongest exchange interaction to occur between two inequivalent vanadium sites via two intermediate oxygen ions. The ESR absorption spectra can be well fitted by a single Lorentzian line and the temperature dependence of the ESR intensity, and the dc susceptibility can be modeled by using the Bloch-Weiss approach for independent dimers. The temperature dependence of the ESR linewidth at X-band frequency can be modeled by a superposition of a linear increase with temperature with a slope $\alpha = 1.35 \text{ Oe/K}$ and a thermally activated behavior with an activation energy $\Delta / k_B = 1418$ K, both of which point to spin-phonon coupling as the dominant relaxation mechanism in this compound.

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I. INTRODUCTION

Spin-dimer systems that form a nonmagnetic singlet ground state at low-temperatures are a fascinating class of materials, which, for example, may undergo a spin-Peierls transition or may be driven to a magnetic-field induced condensation of magnons. Transition metal oxides provide many of the physical realizations of such systems, such as TiCuCl$_3$, BaCuSi$_2$O$_6$, and the systems A$_3$B$_2$O$_8$ ($A = Ba,Sr; B = Cr,Mn$). Here, we investigate the vanadium oxide Sr$_2$VO$_4$, which forms two polymorphic structures: a tetragonal one with an alternating spin-orbital order ground state and an orthorhombic one with a gapped spin-dimer ground state, which will be in the focus of this study. In orthorhombic Sr$_2$VO$_4$, the V$^{4+}$ ions are in a 3d$^1$ configuration and the electron occupies the low-lying e states in tetrahedral environment as sketched in Fig. 1. The material exhibits orthorhombic symmetry with space group Pnma$_1$ and lattice parameters $a = 14.092(2)$ Å, $b = 5.806(2)$ Å, and $c = 10.106(3)$ Å (see Fig. 1). The orthorhombic distortion can be interpreted in terms of a Jahn-Teller distortion, which removes the orbital degeneracy of the V$^{4+}$ ions. No phase transitions have been observed in the temperature range from 4 to 300 K for orthorhombic Sr$_2$VO$_4$. Its susceptibility has been described in terms of a spin-dimer system with a singlet ground state and an antiferromagnetic intradimer coupling of about 100 K. However, a clear identification of the superexchange paths corresponding to the magnetic intradimer coupling is not available at present, because the superexchange paths between the structural VO$_4$ units will involve two or more ligands. Such more complicated super-super-exchange (SSE) paths have been found to yield exchange couplings of considerable magnitude and to determine the ground-state properties in a large number of compounds.

II. experimental details

Here, we investigate orthorhombic Sr$_2$VO$_4$ by magnetization and electron spin resonance experiments. The exchange paths are analyzed by an extended Hückel tight-binding (EHTB) approach and one dominant exchange path via two intermediate oxygen ions is identified. The ESR intensity confirms the dimer approach of the susceptibility, the spin-orbit coupling is estimated from the effective $g$ factor, and the linewidth seems to be governed by a phonon-mediated relaxation mechanism and a thermally activated process.
III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Magnetic susceptibility

Let us now consider the temperature dependence of the molar susceptibility of Sr\(_2\)VO\(_4\) as shown in Fig. 3. The susceptibility has been reported previously by Gong and coworkers who described the system in terms of antiferromagnetically coupled spin dimers with a singlet ground state.\(^{21}\) We follow this approach to analyze the molar susceptibility \(\chi_m\) determined from the magnetization \(M\) measured in an applied magnetic field \(H = 1\) kOe in the entire temperature range and we use

\[
\chi = \chi_0 + \chi_C + \chi_{BB},
\]

with a Curie contribution \(\chi_C = C/T\) (dash-dotted line in Fig. 3) due to unbound spins and magnetic impurities, a temperature independent contribution \(\chi_0\), and the dimer susceptibility \(\chi_{BB}\) as derived by Bleaney and Bowers (BB) (dashed line in Fig. 3):\(^{26}\)

\[
\chi_{BB}(T) = \frac{N g^2 \mu_B^2}{k_B T} \left[ 3 + \exp(J/k_B T) \right]^{-1}.
\]

Here, \(J\) denotes the intradimer exchange coupling, \(g\) is the effective \(g\) factor of the vanadium ions, and \(\mu_B\) is the Bohr magneton. The BB equation is valid in the case \(g\mu_B H \ll k_B T\), i.e., where the Zeeman splitting is small compared to the thermal energy, which is fulfilled in the investigated magnetic field and temperature range. The \(g\) factor was fixed to the experimental value \(g = 1.89\) observed in the X-band ESR measurements with resonance field of the same order of magnitude as the one applied to measure the susceptibility (see below). The obtained fit parameters are \(J = 104\) \(K\), \(\chi_0 = -1 \times 10^{-4}\) cm\(^3\)mol\(^{-1}\), which is of the typical order of magnitude for a diamagnetic contribution, and \(C = 0.028\) cm\(^3\)Kmol\(^{-1}\), corresponding to about 7% unpaired spins. The maximum of the susceptibility is not perfectly described by this fit with a fixed experimental \(g\) value, which might indicate the importance of further exchange couplings between the magnetic dimers. Adding an additional effective interdimer contribution\(^{23}\) with coupling \(J'\) to Eq. (2) leads to an improved fit of the data (not shown), the obtained fit parameters of \(J\) and \(J'\) are, however, of comparable magnitude which in return discards this approach.\(^{27}\) Given the fact that the obtained value for the intradimer exchange \(J = 104\) \(K\) is in agreement with literature\(^{21}\) and corresponds nicely to a magnetic excitation peaked at 8.6 meV observed by neutron scattering,\(^{28}\) we think that the model given by Eq. (1) is presently the best parameterization of the experimental...
structure of Sr$_2$VO$_4$ with space group denoted as V(1) and V(2), respectively. The two crystallographically inequivalent V ions are paths. The large, middle, and small spheres show Sr, V, and O atoms, respectively. The two crystallographically inequivalent V ions are denoted by the path corresponding to the dominant exchange-coupling constant. Therefore we performed an EHTB analysis of the exchange paths, which will be discussed in the following.

**B. Analysis of the exchange paths**

Six distinct exchange paths with exchange couplings $J_0$–$J_5$ and increasing distance between the vanadium ions can be identified in the structure of Sr$_2$VO$_4$ (see Fig. 4 and Table II). The interaction between the magnetic orbitals of two ions in a spin dimer gives rise to two molecular orbitals with an energy splitting $\Delta e$. In the spin-dimer analysis based on EHTB calculations, the strength of an antiferromagnetic exchange interaction between two Van der Waals distances estimated by $J_{AF} = -((\Delta e)^2)/U_{eff}$, where the effective on-site repulsion $U_{eff}$ is taken to be constant. Therefore the trend in $(\Delta e)^2$ is taken as a measure of the $J_{AF}$ values. Double-$\xi$ Slater-type orbitals $\phi_i$ are adopted to describe the atomic $s, p$, and $d$ orbitals in the EHTB calculations, which depend on two exponents $\xi$ and $\xi'$ and coefficients $C$ and $C'$. The atomic parameters used for the EHTB calculations of $(\Delta e)^2$ are summarized in Table I. In the EHTB approach, the effective one-electron Hamiltonian $H_{eff}$ is defined semiempirically by its matrix elements. The diagonal matrix elements are denoted by $H_{ii} = \langle \phi_i | H_{eff} | \phi_i \rangle$. The values of the off-diagonal matrix elements $H_{ij} = \langle \phi_i | H_{eff} | \phi_j \rangle$ were taken from Ref. 32. The parameters of V and O atoms are referred to the previous EHTB calculations on other vanadate compounds, while the rest are taken from the atomic orbital calculations.

As suggested in Ref. 21, the exchange paths between neighboring vanadium atoms could be V–O–O–V or V–O–Sr–O–V. According to our calculations, the interactions between second- to fifth-nearest neighboring pairs of V ions [see Figs. 4(c)–4(f)] are significantly increased, when the strontium atoms are considered in the exchange paths. In contrast, the effect of the strontium atoms is negligible for the exchange path $J_0$ [see Fig. 4(b)]. As shown in Figs. 4(b)–4(f), the solid lines indicate the exchange paths between pairs of V ions corresponding to $J_0$–$J_5$. For $J_1$, the exchange path V–O–V is still important due to the relatively small distance between the V ions. For $J_2$–$J_5$, the exchange paths via Sr ions are more important. Since the distance between sixth nearest neighboring V ions is quite large, the corresponding exchange interaction $J_5$ is quite small as obtained in Table I, which indicates that neither the exchange path V–O–O–V nor the V–O–Sr–O–V gives a significant contribution to $J_5$.

The results of our calculations are summarized in Table II. It shows that the dominant spin-dimer exchange is mediated by the path corresponding to $J_0$ [see Fig. 4(b)], where the

<table>
<thead>
<tr>
<th>atom</th>
<th>$\phi_i$</th>
<th>$H_{ii}$ (eV)</th>
<th>$\xi$</th>
<th>$C$</th>
<th>$\xi'$</th>
<th>$C'$</th>
</tr>
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<tbody>
<tr>
<td>V</td>
<td>4s</td>
<td>−8.81</td>
<td>1.697</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>4p</td>
<td>−5.52</td>
<td>1.260</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>3d</td>
<td>−11.0</td>
<td>5.052</td>
<td>0.3738</td>
<td>2.173</td>
<td>0.7456</td>
</tr>
<tr>
<td>Sr</td>
<td>5s</td>
<td>−6.62</td>
<td>1.630</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>5p</td>
<td>−3.92</td>
<td>1.214</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>2s</td>
<td>−32.3</td>
<td>2.688</td>
<td>0.7076</td>
<td>1.675</td>
<td>0.3745</td>
</tr>
<tr>
<td>O</td>
<td>2p</td>
<td>−14.8</td>
<td>3.694</td>
<td>0.3322</td>
<td>1.825</td>
<td>0.7448</td>
</tr>
</tbody>
</table>

**TABLE II.** Values of the V⋯V distance in Å and $(\Delta e)^2$ associated with the exchange path $J_0$–$J_5$ in Sr$_2$VO$_4$.

<table>
<thead>
<tr>
<th>path</th>
<th>V⋯V</th>
<th>$(\Delta e)^2$ (meV)$^2$</th>
<th>$J_i/J_0$</th>
</tr>
</thead>
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<tr>
<td>$J_0$</td>
<td>4.090</td>
<td>1370</td>
<td>1.00</td>
</tr>
<tr>
<td>$J_1$</td>
<td>4.682</td>
<td>46</td>
<td>0.03</td>
</tr>
<tr>
<td>$J_2$</td>
<td>4.734</td>
<td>210</td>
<td>0.15</td>
</tr>
<tr>
<td>$J_3$</td>
<td>4.978</td>
<td>55</td>
<td>0.04</td>
</tr>
<tr>
<td>$J_4$</td>
<td>5.381</td>
<td>69</td>
<td>0.05</td>
</tr>
<tr>
<td>$J_5$</td>
<td>5.511</td>
<td>15</td>
<td>0.01</td>
</tr>
</tbody>
</table>

FIG. 4. (Color online) (a) Projection of the orthorhombic lattice structure of Sr$_2$VO$_4$ with space group $Pna2_1$ on the $ac$ plane. The exchange paths between neighboring V ions are denoted by the corresponding exchange constants $J_0$–$J_5$ in the sequence of increasing V⋯V distance. (b)–(g) Spin dimers associated with these exchange paths. The large, middle, and small spheres show Sr, V, and O atoms, respectively. The two crystallographically inequivalent V ions are denoted as V(1) and V(2), respectively.

susceptibility. From the structural arrangement, however, it is not clear which of the possible exchange paths corresponds to this dominant exchange-coupling constant. Therefore we performed an EHTB analysis of the exchange paths, which will be discussed in the following.
distance between two V ions is shortest. It is interesting that the second strongest exchange is not between the second-nearest-neighbor V ions, but mediated along the path with \( J_2 \). We want to recall that the exchange constants cannot be fully calculated by the EHTB approach, but the estimate of the relative strength of the exchange coupling \( J_s \) has been found to describe many systems accurately.\(^{22}\) However, the presently available data on polycrystalline Sr\(_2\)VO\(_4\) does not allow to determine subdominant exchange interactions and compare directly to the above estimates.

### C. Electron spin resonance

The absorption spectra of Sr\(_2\)VO\(_4\) both at X-band (\( \nu \approx 9 \) GHz) and Q-band frequencies (\( \nu \approx 34 \) GHz) can be described by an exchange-narrowed Lorentzian line shape as shown in the insets of Fig. 5. The temperature dependencies of the obtained fit parameters are shown in Fig. 5. The experimentally observed effective \( g \) factor at X-band frequency exhibits a constant value of 1.89 in the temperature range 50 < \( T < 200 \) K, while the evaluation of the Q-band spectra results in a higher value of 1.92. This difference is assigned to the fact that the ESR absorption signal in a powder sample is a statistical average over the presumably anisotropic spectra with regard to the orthorhombic crystal axes and the existence of two crystallographically inequivalent vanadium sites (see Fig. 1). At higher resonance frequencies these contributing resonance absorptions will separate more strongly in terms of their respective resonance fields and thus alter the averaged fit parameters obtained by parameterizing the powder spectrum by a single Lorentzian line. The broader distribution of resonance fields also result in an additional broadening of the linewidth via the anisotropic Zeeman interaction\(^{19}\) and, indeed, an increase of the linewidth of about 80 Oe in the Q-band data with respect of the X-band data is observed for temperatures below about 150 K. Above the linewidth values for both frequencies coincide within the experimental uncertainty. We used the value of 1.89 to fit the susceptibility (see Fig. 3), because the applied external magnetic field is comparable to the X-band resonance field of about 0.3 kOe. Accordingly, the temperature dependence of the X-band ESR intensity \( \chi_{\text{ESR}} \) can be well fitted by using Eq. (1) [solid line in Fig. 5(a)] and yields a slightly larger exchange constant \( J = 107 \) K. These parameters are in agreement with the fit for \( \chi_m \) and show that the resonance absorption originates from magnetic dipole allowed intratraplet excitations with \( \Delta S = \pm 1 \) (see inset of Fig. 3). The increase of the \( g \) factor and the decrease of the ESR linewidth below 30 K signal the depopulation of the excited triplet state and the ESR intensity should drop to zero in the ground state. Instead, the intensity increases towards lower temperatures in a Curie-like fashion (solid circles) indicating that the Lorentzian resonance signals at lowest temperatures with \( g = 1.94 \) and \( \Delta H = 156 \) Oe belong to unpaired paramagnetic ions in the sample.

For the intratraplet excitations (open symbols), we find an almost temperature independent \( g \) factor \( g = 1.89 \) between 50 and 150 K. The decrease towards higher temperatures is probably related to the increasing linewidth, which reaches the order of magnitude of the resonance field above 200 K and, hence, imposes a larger uncertainty on the resonance field (or \( g \) factor) as a fitting parameter. In first-order perturbation theory, the effective \( g \) factor is given by

\[
g = 2 - \frac{4\lambda}{\Delta_{\text{CF}}},
\]

with the spin-orbit coupling \( \lambda \) and the \( e - \ell_2 \) crystal-field splitting parameter \( \Delta_{\text{CF}}.\(^{34}\) Using \( g_X = 1.89, g_Q = 1.92, \) and \( \Delta_{\text{CF}} = 8900 \) cm\(^{-1}\) as observed by ellipsometry measurements\(^{15}\) we estimate \( \lambda = 178-244 \) cm\(^{-1}\) (22–30 meV) in agreement with the values obtained for V\(^{4+}\) ions in other compounds.\(^{16,20,34}\)

The temperature dependence of the ESR linewidth \( \Delta H \) of the intra-triplet excitations is shown in Fig. 5(c). The linewidth increases monotonously with temperature, between 50 and 170 K only with a moderate slope but for higher temperatures a strong increase sets in, indicating the presence of further relaxation mechanisms. The temperature dependence can be well described by

\[
\Delta H = \Delta H_0 + \alpha T + Ae^{-\frac{T}{\Theta}},
\]

with \( \Delta = 1418(19) \) K, a residual zero-temperature value \( \Delta H_0 = 593(5) \) Oe, \( \alpha = 1.35(4) \) Oe/K, and \( A = 1.23(7) \times 10^7 \) Oe at X-band frequency. Fitting the linewidth data at Q-band frequency (not shown) yields the parameters

![FIG. 5. (Color online) Temperature dependence of (a) the ESR intensity together with a fit using Eq. (1), (b) the effective \( g \) factor, and (c) the ESR linewidth in Sr\(_2\)VO\(_4\) together with a fit using Eq. (4). The insets show ESR spectra and fit curves with the derivative of a Lorentzian line shape at X-band and Q-band frequencies.](image-url)
\[ \Delta H_0 = 670(25) \text{ Oe}, \alpha = 1.39(22) \text{ Oe/K}, A = 3.1 \pm 1.5 \times 10^7 \text{ Oe, and } \Delta = 2.7 \pm 1.1 \times 10^7 \text{ K}, \] which bear a large uncertainty for the exponential parameters as a result of the more limited temperature range and the enhanced scattering of the data at highest obtained temperatures.

Usually, the ESR linewidth in concentrated paramagnetic systems like Sr\(_2\)VO\(_4\) is related to spin-flip processes governed by anisotropic spin-spin interactions. For diluted magnetic ions in a nonmagnetic host lattice, a linear increase in the linewidth has been discussed as a result of the modulation of the crystal-electric field by a direct one-phonon process, which modulates the spin-spin relaxation processes via spin-orbit coupling. The slope of this linear increase is expected to strongly depend on the applied magnetic field, e.g., \( \propto H^2 \) in the case of diluted Kramers ions.\(^3\) This is clearly not the case for Sr\(_2\)VO\(_4\), where the linewidth at Q-band frequency of 34 GHz (resonance field of about 12 kOe) is only about 80 Oe (10%) larger than the one at 9 GHz (resonance field of about 3.3 kOe) and exhibits a similar temperature dependence. There are only few experimental and theoretical reports on concentrated magnetic systems with a linear linewidth increase and field-independent slope.\(^36\)–\(^41\)

Cox and coworkers suggested a mechanism to explain the linear temperature dependence of the linewidth in Cu(HCOO)\(_2\)·4H\(_2\)O, assuming the existence of so-called exchange spin pockets where the spin-up and spin-down sublevels are mixed by an anisotropic spin-spin coupling exchange parameter \( D \) that cancels the magnetic-field dependence of the slope of the linear linewidth increase with temperature.\(^36\) The nature of these exchange pockets is, however, not specified. The same authors suggested the possibility for the linear temperature dependence of the linewidth without magnetic-field dependence due to spin-phonon coupling via modulation of isotropic exchange interactions, but this idea was seemingly discarded by Gill afterwards.\(^42\)

A second mechanism was suggest by Seehra and Casterner who argued that the linear temperature dependence in concentrated paramagnets can originate from the phonon modulation of the Dzyaloshinsky-Moriya (DM) interaction, which yields a mixing of the different spin states of exchange coupled pairs.\(^37,38\) In this case, the relevant phonon frequency is about \( \propto J/\hbar \) and the one-phonon contribution yields a linear temperature dependence of the linewidth with a slope independent of the value of the magnetic resonance field (or independent of the resonance frequency).

In principle, our results are in agreement with both scenarios, but many details of these two possible mechanisms remain unclear with the former evoking unspecified exchange pockets and the latter assuming a crucial role of the phonon modulated DM interaction for the transition probability between the singlet ground state and excited tripled state. Note that experimentally, we have no indication of the presence of a sizable static DM interaction, but there is no center of inversion between the two inequivalent V sites and a static DM contribution within the dimers could arise.

Moreover, we would like to mention a further possible scenario which is related to a dynamical DM interaction as discussed for KCuF\(_3\).\(^43\) A straightforward way to calculate the ESR linewidth in concentrated paramagnets is the method of moments and it is well known that the isotropic exchange interaction (even it is modulated by phonons) commutes with the total spin and, therefore, can not be responsible for the linear temperature dependence of the ESR linewidth. Thus the focus is on the anisotropic exchange interactions. In contrast to the case of a one-phonon process in diluted magnetic systems, the \( \delta \) function \( \delta(h \omega - g \mu_B H) \) does not appear in the thermodynamic average of the phonon-modulated second moment. Therefore, not only phonons with frequencies \( h \omega_{\text{phon}} = g \mu_B H \) are contributing, but also phonons at higher frequencies, which are closer to the maximum of the phonon density of states. This effect should be related to a local vibrational mode, which modulates the anisotropic exchange contributions or may, for example, induce a dynamical DM contribution as in the case of KCuF\(_3\).\(^43\) In the limit \( h \omega_{\text{ph}} \ll k_B T \) a linear temperature dependence of the linewidth is obtained which is independent of the resonant magnetic field.

A thermally activated contribution has been observed for several low-dimensional magnets\(^3\)\(^,3\)\(^4\)\(^,3\)\(^4\,4\) and in the dimer system Sr\(_2\)Cr\(_2\)O\(_6\), where Cr\(^{5+}\) ions also have an electronic 3d\(^1\) configuration in a tetrahedral crystal field.\(^1\)\(^4\) In the latter compound the value of \( \Delta = 388 \text{ K} \) is within the phonon frequency range and the contribution was tentatively assigned to stem from a two-phonon Orbach process, where the spin relaxation occurs via an absorption of a phonon to a higher-lying electronic state in the energy range of the phonon continuum. For Sr\(_2\)VO\(_4\), the value \( \Delta = 1418(19) \text{ K} \) is too high for phonon modes and rules out the presence of an Orbach mechanism. Since all of the mentioned studies deal with Jahn-Teller active ions, another possible origin of such a thermally activated behavior could be the presence of different Jahn-Teller distortions, which are close in energy, e.g. in case of the one-dimensional magnet CuSb\(_2\)O\(_6\) (Cu\(^{2+}\) with spin 1/2 in octahedral environment) the exponential increase of the linewidth with \( \Delta = 1484 \text{ K} \) has been observed on approaching a static-to-dynamic Jahn-Teller transition at 400 K.\(^42\) The value of \( \Delta \) would then correspond to the energy barrier separating the two Jahn-Teller configurations.

**IV. SUMMARY**

In summary, we investigated orthorhombic Sr\(_2\)VO\(_4\) by electron spin resonance measurements at X- and Q-band frequencies and identified the dominating exchange path to occur between two inequivalent vanadium sites via two intermediate oxygen ions using an EHTB analysis. The temperature dependence of the ESR intensity and the magnetization reveal a dimerized singlet ground state with an intradimer coupling constant \( J/k_B \approx 100 \text{ K} \). The effective g factor \( g = 1.92 \) at 34 GHz (Q band) is slightly larger than the one obtained at 9 GHz (X band), which is assigned to the fact that these values are averages of the g tensors of the two different V sites and the different resonance absorptions are parametrized by a single Lorentzian lineshape. Accordingly, the effective ESR linewidth increases by about 10% when measured at 34 GHz, but at both frequencies the linewidth exhibits an increase with rising temperature, which can be understood in terms of a phonon-modulated spin relaxation yielding a linear increase with slope \( \alpha = 1.35 \text{ Oe/K} \) and a thermally activated Arrhenius behavior with an activation energy \( \Delta/k_B = 1418 \text{ K} \), which might be related to the Jahn-Teller distortion of the system.
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25S. Toth et al. (unpublished).
26Our calculations were carried out by employing the SAMOA (structure and molecular orbital analyzer) program package (M.-H. Whangbo et al., North California State University, http://wwwprime.com/products.htm).
32J. Teyssier et al. (unpublished).