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Proton shift tensors in hydrogen molybdenum bronze

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Résumé. — La forme de la raie R.M.N. du proton, pour une série de bronzes hydrogène molybdène préparés grâce à une méthode chimique en solution, est présentée et comparée avec des résultats précédemment publiés pour des bronzes obtenus en utilisant la méthode dite d'hydrogen spillover. Les résultats montrent que le bronze ainsi formé présente le même spectre R.M.N. du proton que celui trouvé pour H1.6MoO3 préparé par la méthode hydrogen spillover. Le monocristal préparé par la méthode chimique en solution, présente une évidente anisotropie optique. Une étude R.M.N. du proton par rotation du monocristal est donnée.

Bien que la structure détaillée du bronze ne soit pas connue, le repère principal du tenseur peut être relié simplement au repère du cristal de bronze, à la température ambiante. L'inhabituelle dépendance en température des composantes du tenseur est donnée et discutée en termes de propriétés électroniques du solide.

Abstract. — Proton N.M.R. powder pattern lineshapes for a series of hydrogen molybdenum bronzes prepared using a wet chemistry method are presented and compared with published results for bronzes prepared using the hydrogen spillover method. The results demonstrate that a bronze is formed which exhibits the same unusual proton N.M.R. spectra as found for H1.6MoO3 prepared by the hydrogen spillover method. Single crystals prepared by the wet chemistry method exhibit an obvious visual anisotropy. A single crystal 1H N.M.R. rotation study of H1.6MoO3 is reported.

Although the detailed structure of the bronze is not known, the principal axis frame of the tensor can be related simply to the crystal frame of the bronze at room temperature. Unusual temperature dependence of the tensor components is reported and discussed in terms of electronic properties of the solid.

1. Introduction. — Solid state proton N.M.R. has in the past, concerned itself with information which can be obtained from relaxation time studies, second moment analyses, and, more recently, shift information obtained using multiple pulse sequences or magic angle spinning [1-3]. While most solids provide an isotropic powder pattern N.M.R. lineshape because of fast motional averaging, the hydrogen molybdenum bronze studied here does not. Cirillo and Fripiat [4] showed that not only does the bronze produce, at room temperature, a powder pattern characteristic of an axially symmetric tensor; but that the powder pattern linewidth is directly proportional to the field. Thus at room temperature we must conclude that the lineshape is dominated by chemical shift or Knight shift interaction. As the bronze is a fair conductor having a Fermi temperature of about 1.83 x 104 K [5] the spectra could well be due to Knight shift.

Another intriguing aspect of the problem is the fact that the direction of the tensor is opposite to that seen for many proton shift tensors. For example, hydrogen bonded solids usually display a nearly axially symmetric shift tensor for which the unique component is more shielded (at higher field), while for the bronze the unique component appears less shielded.

Furthermore, this bronze has the isotropic value of its shift in the same region of the spectrum as that for systems in which hydrogen are either directly bonded to elements of the first row of the periodic table [1, 2] or are participating in ionic bonding as in the alkaline earth hydrides [6] (σ = 0 to −10 ppm). By contrast, systems which have been studied in which hydrogens directly bonded to transition metals were found to have a positive isotropic shift [3, 7]. In addition, one study of proton N.M.R. in a conducting system showed a rigid lattice axially symmetric tensor for which the direction is like that commonly observed [3]. Of course the proton could be moving from one axially symmetric site to another and if the dipolar contribution is very much motionally narrowed at room temperature, the lineshape produced by the shielding tensor may dominate the overall lineshape. Furthermore, as the temperature is lowered,
the powder pattern lineshape is seen to become non-
axial and by 200 K the line is seen to be symmetric
and to be centred at the room temperature isotropic
position [4]. This temperature dependence was con-
firmed in a multiple pulse study [8].

2. Experimental. — The preparation of polycrystalline \( \text{H}_2\text{MoO}_3 \) by the hydrogen spillover method [4] proceeds in a matter of minutes. Unfortunately, this method does not provide good single crystals for N.M.R. The next method chosen for the preparation of crystals was a wet chemistry method [9] using zinc and HCl but excluding oxygen. This method produced a series of polycrystalline bronzes which were studied by N.M.R. and showed clearly that a bronze of the type \( \text{H}_2\text{MoO}_3 \) could be prepared by the wet chemistry method.

As the powder is prepared in that way it goes
through a series of color changes from a blue to a
to a red green coloration of the essentially black
material. As the spillover bronze is reddish-black in
appearance this provided an additional criterion for
preparation of the desired form. The red form was
studied as a function of temperature and displayed
the same temperature dependence as the bronze
prepared by the spillover method.

For the crystal preparation, single crystals of
\( \text{MoO}_3 \) (about 0.5 \( \times \) 2 \( \times \) 5 mm) were selected as
starting material and oriented loosely in small flat
tubes with the long edge vertical. The crystal was
leached in the tube with a 0.1 N HCl solution contain-
ing Zn powder (Zn/2 H\(^+\) atomic ratio = 1) for 48 h
at room temperature. Afterwards it was washed with
diluted HCl then with water in nitrogen atmosphere.
Finally it was outgassed at 120 °C for 4 hours. The
position of the crystal is illustrated in figure 1a. The
\( C \)-axis of the starting \( \text{MoO}_3 \) single crystal is parallel
to the rotation axis of the tube. Upon formation the
bronze is seen to expand in layers and to fill the pre-
paration tube. The shaded face in figure 1a corre-
ponds to the face which turns dark red as the bronze
is formed. The expansion is so dramatic that, if the
relative sizes of tube and starting material are not
carefully chosen the expanding bronze will shatter
the tube. This layered structure is at the origin of the
obvious optical anisotropy of the resulting material
with the red face perpendicular to the axis of expa-

dision. The other two faces appear black.

Two samples were prepared, and both exhibited the
same rotational dependence for the initial orientation
in the N.M.R. study.

Proton N.M.R. measurements were carried out
using a Bruker SXP pulse spectrometer operating at
90 MHz and having a nitrogen-flow variable tempera-
ture probe. N.M.R. tubes were placed in the probe
perpendicular to the field, and rotation patterns from
0° to 180° were obtained at 18° intervals. Signal
averaging was employed to improve signal to noise.

Due to the fact that the crystal has to be handled
in the sealed tube, there is an obvious lack of accuracy
in the various orientations that were scanned, espe-
cially in the second orientation (Fig. 1b).

3. Results and discussion. — A series of experiments
has been performed which indicates that there is
only one kind of protons for N.M.R. at room tempe-

ture [8]. We cannot say for sure that there are not
multiple sites at lower temperatures. However our
temperature dependent single crystal rotation study
consistently showed one line and suggests one site at
lower temperature. A multiple pulse study capable
of removing homonuclear dipole-dipole interactions
could confirm this observation which is somewhat
obscured at lower temperature by the broadening of
the individual line. As the treatment of the data at
room temperature is unambiguous, it receives the
major emphasis of this report.

Although powder pattern lineshapes can provide
principal values of the shift tensor, a single crystal
study is usually needed in order to assign the direction
of principal axis system (PAS) within the solid. Such
methods are described in detail elsewhere [1]. In
principle, one simply measures the position of the
N.M.R. line with respect to some reference (such as
TMS) as a function of rotation angle. The resulting
rotation pattern is a function of the rotation angle
and of the crystal frame components of the tensor.
If \( \sigma_{zz} \) represents the laboratory frame measurement
we have

\[
\sigma_{zz} = f(\phi, \sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{12}, \sigma_{13}, \sigma_{23})
\]

where \( \phi \) is the rotation angle and the \( \sigma_{ij} \)'s are com-
ponents of the tensor in a crystal fixed frame. The rota-
tion pattern yields the \( \sigma_{ij} \)'s, and diagonalization of the
resulting 3 \( \times \) 3 symmetric matrix yields the PAS
values and the orientation of the PAS with respect to
the crystal frame.

For the simple case in which the PAS coincides
with the crystal frame and, in addition, the crystal
frame axes have been chosen as axes of rotation, the

![Fig. 1. — Crystal orientations. The cross-hatched face represents
the colored face of the crystal. In (a) the rotation is started with
the normal to the red face parallel to the field; (b) shows the ideal-
lized second orientation. In that case the crystal was actually tilted
slightly with the X-axis 10-15° from the vertical.](image-url)
expressions for the laboratory frame variation take
on a particularly simple form. For convenience in
this discussion we choose the trace of the tensor to be
zero. That is, reference frequency is the isotropic
value of the powder pattern line (actually \( \sim -7 \) ppm)
with respect TMS [4]. Then we have for the first
orientation:

\[
\sigma_{zz} = \frac{1}{4}(\sigma_{22} + \sigma_{33}) + \frac{1}{4}(\sigma_{11} - \sigma_{22}) \cos 2 \phi \tag{2}
\]

and for the second orientation:

\[
\sigma_{zz} = \frac{1}{4}(\sigma_{22} + \sigma_{33}) + \frac{1}{4}(\sigma_{22} - \sigma_{33}) \cos 2 \phi . \tag{3}
\]

The results of the experiments are displayed in figure 2.
We can see that, at room temperature, the idealization
taken from the powder pattern line. Lines are drawn through
the data points to aid the eye.

![Figure 2](image_url)

Fig. 2. — Crystal rotation patterns as a function of temperature.
2a corresponds to orientation in figure 1a and 2b corresponds to
1b. The reference frequency (zero ppm) is the isotropic value
taken from the powder pattern line. Lines are drawn through
the data points to aid the eye.

The results of the experiments are displayed in figure 2.
We can see that, at room temperature, the idealization
expressed in (2) and (3) is nearly fulfilled and we
conclude that, within experimental error, the principal
axis system of the tensor coincides with the crystal
fixed frame. As could have been anticipated the unique
component is perpendicular to the red face and thus
to the layers of the crystal. The layers in the bronze
are parallel to the C-axis of the starting MoO₃ crystal.
Deviations from this ideal picture can be accounted
for on the basis of disorientations of the layers,
imperfect orientations of the samples, and the fact
that no bulk susceptibility corrections have been
applied to the data. Thus, values of \( \sigma_{ij} \) read directly
from figure 2 must be taken as a lower limit (Table I).

<table>
<thead>
<tr>
<th>Tensor components</th>
<th>Powder pattern [8]</th>
<th>Rotation pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{11} )</td>
<td>-15 \pm 1</td>
<td>-11 \pm 1</td>
</tr>
<tr>
<td>( \sigma_{22} )</td>
<td>+8 \pm 1</td>
<td>+6 \pm 1</td>
</tr>
</tbody>
</table>

Finally, our temperature dependent rotation studies
at 200 K show that the position of peak is independent
of the orientation of the crystal in the magnetic field
(Fig. 2). This fact suggests an isotropic value for the
shift, in agreement with the multiple pulse powder
spectra (MREV-8) observed by Cirillo et al. [8]. One
must consider the possibility that at room temperature
the shift may be dominated by conduction elec-
trons (Knight shift) while below 240 K the electronic
structure of the material changes [5], and the situation
is further complicated by changes in proton motion.

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