Investigation of the magnetic dipole field at the atomic scale in quasi-one-dimensional paramagnetic conductor Li_{0.9}Mo_{6}O_{17}

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Received 24 August 2015, revised 7 October 2015
Accepted for publication 16 October 2015
Published 16 November 2015

Abstract

We report magnetic dipole field investigation at the atomic scale in a single crystal of quasi-one-dimensional (Q1D) paramagnetic conductor Li_{0.9}Mo_{6}O_{17}, using a paramagnetic electron model and \textsuperscript{7}Li-NMR spectroscopy measurements with an externally applied magnetic field \(B_0 = 9\) T. We find that the magnetic dipole field component \((B_{\text{dip}})\) parallel to \(B_0\) at the Li site from the Mo electrons has no lattice axial symmetry; it is small around the middle between the lattice \(a\) and \(c\) axes in the \(ac\)-plane with the minimum at the field orientation angle \(\theta = +52.5^\circ\), while the \(B_{\text{dip}}\) maximum is at \(\theta = +142.5^\circ\) when \(B_0\) is applied perpendicular to \(b\) (\(B_0 \perp b\)), where \(\theta = 0^\circ\) represents the direction of \(B_0\parallel c\). Further estimation indicates that \(B_{\text{dip}}\) has a maximum value of 0.35 G at \(B_0 = 9\) T. By minimizing the potential magnetic contributions to the NMR spectra satellites with the NMR spectroscopy measurements at the direction where the value of the magnetic dipole field component \(B_{\text{dip}}\) is \(\sim 0\), the behavior of the electron charge statics is exhibited. This work demonstrates that the magnetic dipole field of the Mo electrons is the dominant source of the local magnetic fields at the Li site, and suggests that the unknown metal-‘insulator’ crossover at low temperatures is not a charge effect. The work also reveals valuable local electric and magnetic field information for further NMR investigation as recently suggested (2012 \textit{Phys. Rev. B} \textbf{85} 235128) regarding the unusual properties of the material.

Keywords: quasi-one-dimensional conductor, magnetic dipole field, nuclear magnetic resonance (NMR), electric field gradient (EFG)

(Some figures may appear in colour only in the online journal)
(3D) most recently [6, 11]. Thus it involves an electron dimension- nal crossover [14, 15] and may involve spin triplet Cooper pairs as most recently suggested theoretically [6, 16], with a non-conventional spin triplet (p-wave) superconducting state as one of its potential electron ground states.

Li$_{0.9}$Mo$_6$O$_{17}$ has also been a subject of intensive experimental studies over the last three decades [4, 5]. Many different types of experiments has been performed: x-ray diffraction [17], neutron scattering [14], dc magnetic susceptibility [18–20], resistivity [11, 18, 21, 22], heat capacity [23], thermal expansion [15], thermal conductivity [8, 9, 24, 25], Nernst signal [25], optical conductivity [18], muons spectroscopy [26], scanning tunneling microscope (STM) [3], and angle resolved photo-emission (ARPES) [27]. Many of these experiments are the most recently reported ones [8, 9, 11, 19, 21, 24, 25]. But it still faces tremendous challenges for the understanding of many unknown properties. For example, for the low temperature metal-‘insulator’ crossover at 24 K, x-ray diffraction or neutron scattering shows no evidence of structure phase transition [14, 17], dc susceptibility shows no signs of Curie–Weiss deviation in the electron magnetization [18–20], and heat capacity exhibits negligible associated heat anomaly [23].

Because of these challenges and the limitations in many of these experimental techniques, other capable experimental techniques are highly valuable. For example, most recent theoretical studies on Li$_{0.9}$Mo$_6$O$_{17}$ have strongly suggested [7, 28] the significance of charge and spin fluctuations and correlation which are related to the local electric and magnetic fields arising from the Mo electrons and could be measured at the Mo or nearby atom site like the Li. However, none of above experimental techniques were able to probe them directly at the atomic scale. On the other hand, in terms of a Luttinger liquid (if this is the case), long-range Coulomb interactions among the conduction electrons are expected [1, 2, 7] to be stronger than those in a traditional Fermi liquid. The interaction could induce electron polarizations and thus have a direct impact on the local electric and magnetic fields. Therefore, it is important to investigate the local electric and magnetic field from the Mo electrons. Moreover, the field reveals the sources of the charge and spin dynamics [29, 30] of the Mo electrons.

Nuclear magnetic resonance (NMR) is a well-known versatile local probe capable of directly measuring the local electric and magnetic field including the electron charge and spin statics and dynamics at the atomic scale [29, 30].

In this paper, we report the local field investigation at the atomic scale, both theoretically and experimentally, using a theoretical paramagnetic electron model and $^7$Li-NMR spectroscopy measurements on a single crystal of Li$_{0.9}$Mo$_6$O$_{17}$, with an externally applied magnetic field $B_0 = 9$ T. Since we expect the magnetic dipole field from the paramagnetic Mo electrons to be one of the major sources of the local magnetic field (at least one of them) at the Li site according to the NMR theory [29, 30], the magnetic dipole field is our focus in this investigation.

In fact, magnetic dipole fields that originated from the magnetic dipole moments of the electron spins, including the unpaired spins of the paramagnetic conduction electrons, are of particular interest in various aspects of NMR, including NMR spectroscopy, Knight shift, spin-lattice relaxation, and spin-echo decay rate, especially when the dipolar hyperfine couplings to the electron spins are significant, or when the time scale of their fluctuations matches that of the dynamics for the spin-lattice relaxation or spin-echo decay rates in the materials [29–31]. For example, a NMR spectrum could be inhomogeneously broadened and a Knight shift could have a significant value, due to the contribution of the magnetic dipole fields from the electron spins [29–32]. Similar effect could also be generated by other local field sources at the probe nucleus when they are not negligible [33–35]. Unlike other local field sources, magnetic dipole field is always associated with the size and orientation of the magnetic dipole moments and depends on the displacement from the dipole moments. It can be theoretically calculated based on the structure of the crystal lattice, and can also be experimentally measured by the NMR technique directly.

Our main results are that the magnetic dipole field component ($B_{\text{dip}}$) parallel to $B_0$ from the Mo electrons at the Li site is found to have no lattice axial symmetry; it is small around the middle between the lattice $a$ and $c$ axes in the $ac$-plane, with the minimum and maximum to be at $\theta = \pm 52.5^\circ$ and $\pm 142.5^\circ$, respectively, when $B_0$ is applied perpendicular to $b$ ($B_0 \parallel b$) (note, $\theta$ is the orientation angle of $B_0$ relative to the lattice $c$-axis here, and $\theta = 0^\circ$ represents $B_0 \parallel c$). Our further estimation indicates that the maximum value of $B_{\text{dip}}$ at the Li site is $\sim 0.35$ G when $B_0 = 9$ T $\perp b$. By minimizing the potential magnetic contributions to the NMR spectra satellites with the NMR spectroscopy measurements at the direction where the value of the magnetic dipole field component $B_{\text{dip}}$ is $\sim 0$ (close to be the smallest), the behavior of the electron charge statics is exhibited.

This work demonstrates that the magnetic dipole field from the Mo electrons is the dominant source of the local magnetic fields at the Li site, and suggests that the unknown metal-‘insulator’ crossover at low temperatures is not a charge effect. The work also reveals valuable local electric and magnetic field information for further NMR investigation, as recently suggested [28], regarding the unusual properties of this Q1D material.

The rest of the paper is organized as follows. First, section II presents the result of our magnetic dipole field calculation at the atomic scale in the Q1D paramagnetic conductor Li$_{0.9}$Mo$_6$O$_{17}$. The details of the calculation can be found in the appendix A at the end, which is described in a general form manner so that the method can be used for applications in other electron systems. Second, section III shows the comparison with our NMR experimental observations of the magnetic dipole field when a single crystal Li$_{0.9}$Mo$_6$O$_{17}$ sample is exposed to an externally applied magnetic field $B_0$. Third, section IV exhibits the details of the corresponding NMR experiment regarding the electron charge statics. Fourth, section V presents discussions regarding the electron model used in the calculation, and our theoretical approximation of related physics quantities, including the nuclear quadrupolar frequency ($\nu_Q$), a measure of the electric...
With the experimental set-up shown in figures 1(b) and (c), which displays the orientation of $B_0$ using the standard spherical coordinates (angles $\theta$ and $\phi$) in the Cartesian $xyz$-system and the fixed arrangement of the sample crystal lattice $a$, $b$ and $c$ axes in the lattice $abc$-system relative to the $x$, $y$ and $z$ axes in the Cartesian $xyz$-system, respectively, the magnetic dipole field at the Li site from the Mo electrons (of the Mo atoms located at the Mo sites in the crystal lattice) can be calculated using a paramagnetic electron model (see details in the appendix A), based on the crystal structure of Li$_{0.9}$Mo$_6$O$_{17}$ as shown in figure 1(d) (with all the atoms in a single unit cell).

As seen from figure 1(d), the crystal structure of Li$_{0.9}$Mo$_6$O$_{17}$ is built of slabs in the $bc$-plane. The slabs consist of sharing corners of Mo$_4$ octahedra separated by Mo$_2$ tetrahedra and the Li ions along the $a$-axis [10, 17], where the Li ions are located at the large vacant sites between the slabs. Along the $b$-axis, there is a double zig-zag ...Mo1-O11-Mo4-O11... chain [10, 14, 17, 38] which is known to be the most conducting (i.e. the $b$-axis is the conducting axis) (note, the ratio of the electrical conductivity along the $a$, $b$ and $c$ axes is 250 : 10 : 1) [12, 13, 15, 21]. More details of the structure are known from the neutron scattering [14] and/or x-ray diffraction experiments [17].

Figure 2 exhibits the result of the calculation of the magnetic dipole field components at the Li site due to the paramagnetic Mo electron moments in Li$_{0.9}$Mo$_6$O$_{17}$, with vertical axes plotted as $H_x/M$, $H_y/M$, and $H_z/M$ versus $\theta$ and $\phi$ (in arbitrary units by leaving out the constant 1/4\pi in front, for convenience) along the $x$, $y$, and $z$ directions, respectively, where $M$ is the magnitude of the sample magnetization, and $H_x$, $H_y$, and $H_z$ are the $x$, $y$, and $z$ components of the calculated magnetic dipole field intensity, respectively (see equations (A.5)–(A.7) in the appendix A).

Figure 1. (a) Cartesian coordinate system, where an electron magnetic dipole moment $\vec{\mu}_j$ is at the atom site $M$ near the field observation site P in the crystal lattice. (b) The orientation of the externally applied magnetic field, $\vec{B}_0$. (c) A fixed set-up of the Cartesian $x$, $y$, and $z$ axes relative to the $a$, $b$, and $c$ axes of the crystal lattice in the lattice coordinate system that can always be made, where the $xz$-plane is in the $ac$-plane and the $z$-axis is along the $c$-axis. (d) The crystal structure of Li$_{0.9}$Mo$_6$O$_{17}$, with all the atoms in a single unit cell seen near along the $b$-axis. The atoms are labeled in colors.

The corresponding two dimensional (2D) contour plots are shown in the $(\theta, \phi)$ plane, which consist of isolines (on each line the values are the same, while different lines have different values) and areas in different colors according to their values of $H_x/M$, $H_y/M$, and $H_z/M$ as the functions of $\theta$ and $\phi$.

Figure 2 shows that each field component has a rather strong angular dependence on the direction of $\vec{B}_0$, a typical character of a dipolar field as can be seen from equation (A.6). Typical angle of interest here related to our $^7$Li-NMR measurements is at $\phi = 0^\circ$, i.e. when $\vec{B}_0 \perp b$ ($\vec{B}_0$ is in the $xz$- or $ac$-plane).

When $\vec{B}_0 \perp b$, figure 2 shows that the minimums for $H_x$, $H_y$, and $H_z$ are at $\theta = +340^\circ$, $+30^\circ$, and $+130^\circ$ (angle $\theta_{\text{min}}$), respectively, while the corresponding maxima are at $\theta = +160^\circ$, $+210^\circ$, and $+310^\circ$ (angle $\theta_{\text{max}}$), respectively. Thus, none of these field components has an axial symmetry since neither of its maximum nor of its minimum is along the $a$ or $c$ axis in the crystal lattice, which has an angle [17] $\theta = 0^\circ$ and $+90.6^\circ$, respectively. This non-axial symmetry character is also seen in the field component parallel to the externally applied magnetic field $B_0$, as shown in figures 3–4.

Figure 3 shows the result of the calculated magnetic dipole field component parallel to $B_0$ (figure 3(b)), as compared with the magnitude of the magnetic dipole field (figure 3(a)) at the Li site, due to the paramagnetic Mo electron moments in Li$_{0.9}$Mo$_6$O$_{17}$. They are obtained based on the result shown in figure 2, and plotted as $H_x/M$ and $H_z/M$ versus $\theta$ and $\phi$.
respectively, with mathematical expressions for them as,

\[ H_0 = H - (\mathbf{I} \mathbf{B}_0) = H_x \sin \theta \cos \phi + H_y \sin \theta \sin \phi + H_z \cos \phi, \]

and

\[ H = \sqrt{H_x^2 + H_y^2 + H_z^2}. \]

Correspondingly, the 3D contour plots for the values of \( H/M \) and \( H_0/M \) are shown in the \((\theta, \phi)\) plane (figure 3).

Figure 3 indicates that \( H_0 \) and \( H \) have similar angular dependence with \((\theta, \phi)\) to the axial dipolar field intensity components \( H_x, H_y \) and \( H_z \), while their periods with both of the \( \theta \) and \( \phi \) dependence are essentially half of those for the axial dipolar field intensity components, as a result of their combinations (see their expressions above).

One aspect for the importance of the \( H_0 \) component (or \( B_{\text{dip}}^{\text{par}} \)) is that the Knight shift of a NMR spectrum only comes from the contributions of the parallel components of the internal magnetic field sources (i.e. the local field components parallel to \( \mathbf{B}_0 \)), under the high field limit \( (B \ll B_0) \). Here we have the magnetic dipole field \( B = \mu_0 H \), and \( B_{\text{dip}}^{\text{par}} = \mu_0 H_k \).
magnetic dipole field at the Li site that comes from the paramagnetic Mo-electron dipole moments in Li$_{0.9}$Mo$_6$O$_{17}$ (as seen from figure 4).

Interestingly, figure 4 indicates that 1) $B_{\text{dip}}^0$ has the same maximum value as $B$ (with $\max(H/I/M) = \max(H/M) = 0.24$ (arb.unit)), whereas their minimum values are very different, 2) the angles for their values in maximum are the same and the angles for their values in minimum are also the same; their maximum and minimum values are at $\theta' = +52.5^\circ \pm 180^\circ$ and $\theta' = -37.5^\circ \pm 180^\circ$ (i.e. $\theta = +142.5^\circ \pm 180^\circ$ ($\theta_{\text{max}}$) and $\theta = +52.5^\circ \pm 180^\circ$ ($\theta_{\text{min}}$)), respectively, and 3) a range of angles for the small values of $B_{\text{dip}}^0$ (or $H$) is at the angles around the middle between the $a$ and $c$ axes in the $ac$-plane (i.e. at $\theta' \approx -40^\circ \pm 30^\circ$, or $\theta' \approx 50^\circ \pm 30^\circ$) (the minimum is 7.5$^\circ$ closer to the $a$-axis than to the $c$-axis).

In other words, at the angles closer to the $a$-axis, the values of $B_{\text{dip}}^0$ ($H_0$) are $\sim$ zero, and there is no axial symmetry for $B_{\text{dip}}^0$ (or $H_0$) as described above, observing from the Li site.

IV. Details of the corresponding $^7$Li-NMR experiment

High quality single crystals of Li$_{0.9}$Mo$_6$O$_{17}$ were grown using a temperature-gradient flux method [4, 5, 15], and a series of experiments have been conducted on these crystals by Neumeier’s group [14, 15, 22] and Cohn’s group [8, 9, 25]. The sample used for our $^7$Li-NMR measurement has a size $\sim$1.7 mm $\times$ 0.5 mm $\times$ 0.1 mm, which has a mass $\sim$1.5 mg. The NMR coil for the sample was made from 50 $\mu$m diameter copper wire wound with $\sim$30 turns. The sample was fixed on the goniometer in the NMR probe during the measurements so that it can rotate around the lattice $b$-axis. The $^7$Li-NMR experiments were conducted with a spectrometer and probe built at UCLA by Clark’s group.

Figure 5 shows the result of the measured $^7$Li-NMR spectra of Li$_{0.9}$Mo$_6$O$_{17}$, with $B_0 = 9$ T along and the lattice $c$-axis, i.e. $\phi = 0^\circ$ and $\theta = 90^\circ$ (or $\theta' = 0^\circ$), at typical temperatures $T = 275$ K, 78 K, 24 K and 6 K, as an example, plotted as the $^7$Li-NMR free-induction decay (FID) absorption amplitude versus frequency shift (a shift from the NMR Larmor frequency $\nu_0 = \gamma g B_0 = 148.95 \times 10^3$ kHz here, where $\gamma_{^7}\mathrm{Li} = 16.547$ MHz T$^{-1}$ is the gyromagnetic ratio of the $^7$Li nucleus).

For comparison, the spectra are normalized in a standard manner for the intensity of the central line and re-shifted on top of each other (after we obtained the actual shift of the spectrum central line). Since $^7$Li is a spin $I = 3/2$ nucleus, theoretically, each $^7$Li-NMR spectrum is expected to have a central line plus two symmetric quadrupolar satellites due to the $^7$Li nucleus spin quantum $m = +1/2 \leftrightarrow -1/2$ (central) and $\pm3/2 \leftrightarrow \pm1/2$ (satellites) transitions, respectively. This is exactly what we experimentally see here, verifying that all the Li sites are structurally equivalent with a high quality sample being used [37].

Figure 5 indicates that the width of the $^7$Li-NMR spectrum central line, i.e. the full width at half maximum (FWHM),

![Figure 4](image-url)

Figure 4. Calculated (‘calc.’) magnetic dipole field magnitude ($B$) (blue dots/curve) and magnetic dipole field component parallel to $B_0$ ($B_{\text{dip}}^0$) (red dots/curve) at $T = 275$ K at the Li site in Li$_{0.9}$Mo$_6$O$_{17}$ as compared with the experimental (‘exp.’) data, as a function of the angle $\theta'$ (for convenience, we shift the angle $\theta$ by $-90^\circ$ in the following experimental data description), as compared with the measured values at two temperatures $T = 275$ K and 78 K, which are obtained from the angular dependence of the $^7$Li-NMR spectrum central line frequency shift in our $^7$Li-NMR spectroscopy measurements (see next section). As we can see, the calculated result matches well with the experimental data with the consideration of the experimental error ($\leqslant$8%).

Here considering the unit (arbitrary) of $H/I/M$ shown in figures 2–3 and the equations (A.5)–(A.7) (see the appendix A), we have a convenient expression for the values of $B_{\text{dip}}^0$ shown in figure 4 as

$$B_{\text{dip}}^0 = \chi B_0 \cdot (H/I/M).$$  \hspace{1cm} (2)

Similar expressions can also be used for the dipolar field magnitude $B$ and the values of the corresponding axial components $B_a, B_b$ and $B_c (B = \mu_B H)$, where the unit of $B$ is in Gauss (G) or tesla (T) ($1 \text{T} = 10^4 \text{G}$).

As an example, when the applied magnetic field $B_0 = 9$ T with its direction angles $\phi = 0^\circ$ and $\theta = +142.5^\circ$ (or $\theta' = +52.5^\circ$), using the value of $H/I/M = 0.24$ shown in figure 3 and the value of $\chi (300 \text{K}) \approx 0.6 \times 10^{-4} \text{ cm}^3 \text{ mol.FU}^{-1}$ (see section V.B) (note, FU $\equiv$ formula unit), equation (2) gives $B_{\text{dip}}^0 \approx 0.35 \text{ G}$. Obviously, this is the maximum (anisotropic)
On the other hand, a NMR spectrum line can have a mixture of many different sources of internal electric and/or magnetic field contributions (section V.C). According to the NMR theory [29, 30], the satellites and the central line of an NMR spectrum have completely different origins: the central line is dominantly magnetic, due to the contribution of the nuclear spin interaction with the electron spins and other sources of the local magnetic fields, while the satellites are quadrupolar, due to the contribution of the nuclear quadrupole moment (Q) interaction with the electric field gradient (EFG) at the probe nucleus under the high field limit.

Generally, the EFG at a probe nucleus comes from the surrounding effective charges at all the lattice site (called the contribution of the ligand lattice), plus the contributions of the electron orbital overlaps and covalence contributions (called valence contribution), according to the well-known point charge model [29, 30], i.e. the satellites are electronic in origin. Note, the quadrupolar interaction contribution to the frequency shift of the NMR spectrum central line is in the second order and thus usually negligible, depending on the ratio of the square of the nuclear quadrupolar frequency ($\nu_Q$) over the Larmor frequency ($\nu_L$). But its contribution to the frequency shift of the NMR spectrum satellites is in the first order and thus often dominant.

Because of these differences, remarkably, an NMR spectrum satellite of a probe nucleus can be used as a direct probe observing the electron charge statics, which is purely an intrinsic electronic behavior.

However, an NMR spectrum satellite can be both electronically and magnetically broadened, and thus very often we could have a similar angular dependence of its linewidth to that of the NMR spectrum central line. Therefore, in terms of judging the charge contributions by an NMR spectrum satellite, it is important to separate or minimize any potential magnetic contributions in any way possible.

This is exactly why we have the $^7$Li-NMR spectrum measurements here as a function of temperature at the direction along the $a$-axis (figure 5), where the magnetic dipole field component parallel to $B_0$ ($B_{0\parallel}$) is $\sim$ zero (close to the minimum) (figure 4). This is also one of the striking significances that we do the magnetic dipole field calculations in this investigation.

Figure 6 shows the angular dependence of the $^7$Li-NMR spectrum satellite frequency shift, plotted as the values of $\nu_{\parallel}$ and $\nu_\perp$ versus $\theta'$ at various temperatures with $B_0 = 9 T\parallel b$, where $\nu_{\parallel}$ and $\nu_\perp$ corresponds to the positions of $^7$Li-NMR spectrum satellites $P_{\parallel}$ and $P_{\perp}$ in frequency (figure 5), respectively. For comparison, the angular dependence of the calculated magnetic dipole field $B_{\parallel}^{\text{mip}}$ is also displayed together, which shows a similar angular dependence but with its values of maximum and minimum at completely different angles (positions): $B_{\parallel}^{\text{mip}}$ has a shift of $+52.5^\circ$ in angle from the $a$-axis.

Moreover, a nuclear quadrupole interaction with the EFG under the high field limit produces a first-order quadrupolar frequency shift $\nu_\parallel$ to the NMR spectrum satellite describable as [29, 30]

$$\nu_\parallel = k \frac{Q}{I(I+1)}$$

where $Q$ is the nuclear quadrupole moment, $I$ is the nuclear spin quantum number, and $k$ is the coupling constant.

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The angular dependence of the $^7\text{Li}$-NMR spectrum satellite frequency shift of Li$_{0.9}$Mo$_6$O$_{17}$ at various temperatures with $B_0 = 9\, T \perp b$. The dashed red curve is the fit to equation (3). The vertical dotted and dashed lines with labels are for the position of the magic angle and the directions for the $a$- and $c$-axes and the principle axis $Z$ (also the direction of the quadrupole moment component $p_z$) of the EFG, respectively, which are determined from the fit of the data. For comparison, the angular dependence of the magnetic dipole field $B_{\text{dp}}$ is also shown (green curve).

$$\nu_s = \pm \frac{\nu_0}{2}(3\cos^2\theta'' - 1) \pm \eta \frac{\nu_0}{2}\sin\theta'' \cos(2\phi),$$

where $\nu_0 \equiv \frac{eV_{\text{EFG}}}{2\hbar}$.

associated with the spin quantum $m = \pm 3/2 \leftrightarrow \pm 1/2$ transition for the spectrum satellites of a spin $l = 3/2$ nucleus as the $^7\text{Li}$ is. Here we can see (equation (4)) that the nuclear quadrupolar frequency $\nu_0$ is a direct measure of the EFG (tensor $V_{zz}$).

$h$ is the Planck constant, $e$ is the absolute value of the electron charge, $Q$ is the nuclear quadrupole moment (a constant), and $\eta$ is the EFG asymmetry parameter: $\eta \equiv \left| \frac{V_{xx} - V_{yy}}{V_{zz}} \right| (0 \leq \eta \leq 1)$, where $V_{xx}$, $V_{yy}$, and $V_{zz}$ are the components of the EFG tensors along the principal axes $X$, $Y$, and $Z$, respectively. The EFG tensors must satisfy $V_{xx} + V_{yy} + V_{zz} \equiv 0$. $\theta''$ and $\phi$ are the standard spherical angles of $B_0$, where $\theta'' = \theta = 0^{\circ}$ is for $B_0 \parallel Z$. A more general form of equation (4) can be found in the Discussion section V.D, together with theoretical estimation for the value of $\nu_0$ (EFG).

Noticeably, the data of the angular dependence of the $^7\text{Li}$-NMR spectrum satellite frequency shift shown in figure 6 can be well fitted by equation (3). With the consideration of the experimental set-up, the fit gives an experimental value of $\nu_0 = 44.0 \pm 0.5$ (kHz), $\eta = 0$ (within experimental error), $\theta'' = \theta = 90^{\circ}$, and $\phi = 0^{\circ}$ (note, $\phi$ can be determined separately with the experimental set-up).

The effectiveness of this fit can also be seen by the position of the ‘magic angle’, which corresponds to the angle satisfying $3\cos^2\theta'' - 1 = 0$, i.e. $\theta'' = 54.7^{\circ}$ (from the $a$-axis).

This is the angle where $\nu_{s1}$ and $\nu_{s2}$ come across at, i.e. all the spectrum lines including the central line meet on top of each other, $\nu_{s1} = \nu_{s2} = 0$ here (figure 6). Thus, the lattice $a$-axis is the $Z$-component of the principal axis of the EFG tensors. For clarity, the positions of these parameters are indicated in figure 6.

Figure 6 also indicates a highly symmetric satellites ($|\nu_{s1}| = |\nu_{s2}|$) at all temperatures, and there is no signature of any change in the value of $\nu_0$ or EFG upon cooling in temperature.

Figure 7 shows the angular dependence of the $^7\text{Li}$-NMR central linewidth $\Delta \nu_{\text{c}}$ (FWHM) for the central line at $T = 78\, K$ and $24\, K$ with $B_0 = 9\, T \perp b$. The linewidth for the satellites is similar (thus not shown here). As we would expect, the angular dependence of the linewidth $\Delta \nu_{\text{c}}$ can be described as

$$\Delta \nu_{\text{c}} = C_1[3\cos^2\theta'' - 52.5^{\circ} - 1] + C_2(1 - \cos^2\theta'')(1 - 9\cos^2\theta') + C_3,$$

where the 1st term represents the magnetic dipole field contribution, the 2nd term comes from the second-order quadrupolar interaction, and the 3rd term is the residual linewidth. The residual linewidth is independent of the angle $\theta'$, which could be most possibly due to inhomogeneity of the particles in the solid form (not due to the spin-echo decay rate) [29].

The constants $C_1$, $C_2$ and $C_3$ in front of the terms are the fit parameters.

As shown by the dashed lines in figure 7, the data fit to the equation (5) rather well, from which we have the fitted constants $C_1 \approx -0.35\, \text{kHz}$, $C_2 \approx +0.60\, \text{kHz}$, and $C_3 \approx +3.1\, \text{kHz}$. This suggests that the angular dependence of the linewidth is due to both of the dipolar coupling to the Mo electron spins and the quadrupolar interaction with the EFG, as we expected [30].
It is important to notice that the angular dependence of the $^7$Li-NMR linewidth data shown figure 7 further indicates that the magnetic dipole field contribution to the $^7$Li-NMR spectrum linewidth (including that of the satellites) at the angle $\theta' = 90^\circ (\theta = 90^\circ)$, i.e. at the a-axis, is $\sim 0$. Thus, this linewidth data also agrees well with the result of the theoretical calculation (figure 4), which shows the magnetic dipole field component parallel to $B_0$, $B_0^{||}$ is $\sim 0$, at the same angle $\theta' = 90^\circ$ (near the a-axis).

Therefore, the magnetic contribution to the $^7$Li-NMR spectrum lines including that to the satellites (magnetic broadening) can be minimized along the applied magnetic field $B_0^{||} \sim a$-axis, with which it allows the behavior of the EFG including the distribution of EFG, to be investigated separately.

Figure 8 exhibits the $T$-dependence of the $^7$Li-NMR quadrupolar frequency $\nu_Q$ (EFG) and the distribution of $\nu_Q$ (EFG). The later is obtained from the width (FWHM) of the $^7$Li-NMR spectrum satellites with $B_0 = 9T || a$, where the total internal magnetic field at the Li site is $\sim 0$ (section V.C).

Figure 8 shows that there is no signature of change in the value of $\nu_Q$ (EFG) or in the distribution of it, upon cooling over a wide range of temperature from 300 K down to 2.3 K, including at the metal-‘insulator’ crossover temperature $\sim 24$ K. This indicates that there is no appearance of any charge effect anomaly during the cooling process, thus suggesting that the metal-‘insulator’ crossover at low temperatures is not a charge effect.

**V. Discussion**

In this section, we have discussions regarding the paramagnetic electron model and the Pauli spin susceptibility ($\chi_p$) of the Mo electrons used in the calculation, the major sources of the local magnetic fields at the Li site, and our theoretical estimation of the $^7$Li-NMR quadrupolar frequency $\nu_Q$ (EFG).

**V.A. Paramagnetic electron model used in the calculation**

The method used for the magnetic dipole field calculation involves a summation of the magnetic dipole fields from the average of the individual magnetic dipole moments of the electron spins in the crystal lattice in component forms. The calculated dipolar field value converges with the increase of the number $N$ (up to 100) for the amount of the unit cells to be included, within a spherical distance centering at the observation atom (or nucleus) site, which is the Li in this study. It also involves a general matrix transform corresponding to a fixed set-up of the Cartesian $x$, $y$, and $z$ axes relative to the $a$, $b$, and $c$ axes of the crystal lattice in the lattice coordinate system that can always be made.

We have used similar method for the calculation of the magnetic dipole field from the Fe$^{3+}$ ions at the proton sites in the paramagnetic organic conductor $\lambda$-(BETS)$_2$FeCl$_4$ (also a superconductor) [32].

Here we would like to point out that, in the paramagnetic electron model used for the calculation, possible differences of the electron moments among the six independent Mo sites in the structure are not considered. Instead, we use their average magnetic dipole moments as reflected by the magnetization $M$ or magnetic susceptibility $\chi$ (equations (A.4)–(A.5)). We also neglect the individual spin interactions among the Mo electrons. Note, the interaction could polarize the electron dipole moments, which could also be reflected by the susceptibility data $\chi$ (section V.B).

The result of the calculation matches rather well with our $^7$Li-NMR experimental observation, while it is still worthwhile to notice possible difference in the electron moments and potential electron interactions, especially considering that some of the Mo electrons may not be equally conducting (or not conducting) according to their positions in the crystal lattice.

In fact, along the b-axis each of the zig-zag ...Mo1-O11-Mo4-O11... chains [10, 17, 38] involves only 2 (i.e. Mo1 and Mo4) out of 6 independent Mo sites (Mo1, Mo2,..., Mo6) that are believed [15, 21, 38] to have the electrons being the most conducting (conduction electrons), above the metal-insulator cross-over temperature at $T_{MI} = 24$ K [4, 18]. Below $T_{MI}$, recent studies shows that there is a gradual dimensional cross-over [14], and finally Li$_{0.9}$Mo$_6$O$_{17}$ becomes a 3D superconductor at $T \leq 2.2$ K upon cooling with $B_0 = 0$ or $0 < B_0 < \mu_0H_{c2}$ (upper critical field) [11, 16].

However, there is no clear evidence of anisotropy in the dc magnetic susceptibility ($\chi_{dc}$) which could reflect the difference in the electron moments and spin polarizations in Li$_{0.9}$Mo$_6$O$_{17}$. The difference between the axial values of $\chi_{dc}$ that Matsuda et al showed [20] is actually rather small, which is very different from the high anisotropy character in its electrical properties [11, 15, 22].
V.B. Pauli spin susceptibility ($\chi_s$) of the Mo electrons

It is well-known that the Pauli spin (paramagnetic) susceptibility $\chi_s$ comes from the contributions of the conduction electron spin moments only, [39] and the dc magnetic susceptibility ($\chi_{dc}$) has a general expression as $\chi_{dc}(T) = \chi_{dia} + \chi_s(T) + \chi_{orb} + \chi_{other}(T)$, where $\chi_{dia}$ and $\chi_{orb}$ are $T$-independent diamagnetic susceptibility and orbital susceptibility, respectively. The term $\chi_{other}(T)$ comes from other sources, including the localized electron moments, and lattice imperfection and/or impurities, which could be also part of a Curie/Curie–Weiss paramagnetic contribution term and become dominant at low $T$.

The dc magnetic susceptibility ($\chi_{dc}$) measurements in Li$_{0.9}$Mo$_6$O$_{17}$ show that [18, 40]

$$\chi_{dc} = \frac{C}{T + \theta_0} + \chi_0, \quad (T < 100 \text{ K}) \quad (6)$$

and

$$\chi_{dc} \approx (0.30 - 0.40) \times 10^{-4} \text{ (cm$^3$ mol.$^{-1}$F.U.$^{-1}$)}, \quad (100 \text{ K} < T \leq 300 \text{ K}) \quad (7)$$

i.e. it has a Curie–Weiss susceptibility term appears at low temperatures ($T < 100 \text{ K}$), where the Curie–Weiss constant $C = (7.8 \pm 0.2) \times 10^{-4} \text{ cm}^3\text{mol.$^{-1}$K}$, $\theta_0 = (6.1 \pm 0.2) \text{ K}$, and $\chi_0 = (0.181 \pm 0.005) \times 10^{-4} \text{ cm}^3\text{mol.$^{-1}$F.U.$^{-1}$}$. In the high temperature regime ($T \geq 100 \text{ K}$), $\chi_{dc}$ has a value from $\sim 0.40 \times 10^{-4} \text{ cm}^3\text{mol.$^{-1}$F.U.$^{-1}$}$ at 300 K to $\sim 0.30 \times 10^{-4} \text{ cm}^3\text{mol.$^{-1}$F.U.$^{-1}$}$ at 100 K (equation (7)), i.e. it slowly decreases with a very weak $T$-dependence (close to linear here) upon cooling as expected for a quasi-1D conductor, where the $T$-dependence could have a contribution from the Pauli spin susceptibility $\chi_s(T)$ (note, $\chi_s$ has $T$-dependence for a 1D or 3D conductor) [41].

From the diamagnetism of the ions, we have $\chi_{dia} = -2.62 \times 10^{-4} \text{ cm}^3\text{mol.$^{-1}$F.U.$^{-1}$}$, and according to the estimate [20] by Matsuda et al, $\chi_{orb} \approx 2.0 \times 10^{-4} \text{ cm}^3\text{mol.$^{-1}$F.U.$^{-1}$}$. But it seems impractical [19] to have further separations among the susceptibility data so that we can obtain the value of $\chi_s(T)$ directly from the dc susceptibility measurement.

Alternatively, most recent specific heat measurement [19] resulted in $\chi_s(T)$ at $T \rightarrow 0 \text{ K}$ as, $\chi_s(0) = 3.0 \times 10^{-6}$, i.e. $0.50 \times 10^{-4} \text{ cm}^3\text{mol.$^{-1}$F.U.$^{-1}$}$ (a factor with the molar density $\rho = 0.0595 \text{ cm}^3\text{mol.$^{-1}$}$ for Li$_{0.9}$Mo$_6$O$_{17}$), using the measured Sommerfeld constant $\gamma_S = 1.6 \text{ mJ mol.$^{-1}$K.$^{-2}$}$ and the assumption of the Sommerfeld-Wilson ratio [19, 28] $R \approx 4\pi^2 k_B^2 \chi_s(0)/(3g_\text{B}^2 m_\text{B} \gamma_S)^2 = 2$, which applies for strongly correlated electrons and/or systems with repulsive interactions (here $\mu_B$ is the Bohr magneton, $k_B$ is the Boltzmann constant and $g$ is the Lande $g$-factor). Thus based on the measured values of $\chi_s(T)$ (equations (6)–(7)), we can also estimate the value of $\chi_s(T)$ at $T = 300 \text{ K}$, $\chi_s(300 \text{ K}) \approx 3.6 \times 10^{-6}$, i.e. $0.60 \times 10^{-4} \text{ cm}^3\text{mol.$^{-1}$F.U.$^{-1}$}$.

Noticeably, $\chi_s$ is just slightly larger than the high temperature value of $\chi_{dc}$. This is due to the cancellation of the orbital susceptibility $\chi_{orb}$ with the diamagnetic susceptibility $\chi_{dia}$, both of which are $\sim (5–6)$ times larger than the high temperature value of $\chi_{dc}$.

Now, with the value of $\chi_s(0)$ we can find the density of state (DOS) $D(E_F)$ at the Fermi energy ($E_F$) level [41, 39],

$$D(E_F) = \chi_s(0)/\mu_B^2 \approx 1.5 \text{ (state eV.FU.$^{-1}$)},$$

$$\approx 0.25 \text{ (state eV.ion.$^{-1}$)} \quad (8)$$

This value is close to the result obtained from the specific heat measurements, which is $D(E_F) = 3 N_e \epsilon/(\pi^2 k_F^2) \approx 0.68 \text{ (state eVion.$^{-1}$)}$, where $N$ is the number of ions per unit cell, and $e$ is the electron charge [39].

Correspondingly, the value of $E_F$ (at $T \rightarrow 0$) is [41]

$$E_F = d/|2D(E_F)| \approx 6.0 \text{ (eV)},$$

where $d$ is the dimension for the conduction electrons. Here we had $d = 3$ for Li$_{0.9}$Mo$_6$O$_{17}$ as it becomes a 3D conductor (superconductor) at $T \rightarrow 0 \text{ K}$; both equations (8) and (9) are for 3D (not 1D) electrons. In comparison, this value of $E_F$ is slightly smaller than that of the free Cu electrons which has a value [39] of $E_F = 7.8 \text{ eV}$.

V.C. Major sources of the local magnetic fields at the Li site

The Hamiltonian ($H_1$) of the system for the $^7$Li-NMR in Li$_{0.9}$Mo$_6$O$_{17}$ can be expressed as [29]

$$H_1 = H_{iz} + H_{ii} + H_{il}^d + H_{il}^{contact} + H_{dem} + H^{lor}, \quad (10)$$

where $H_{iz}$ is the Zeeman Hamiltonian of the $^7$Li nucleus in $B_0$, $H_{ii}$ is the $^7$Li–$^7$Li nuclear dipolar interaction Hamiltonian, $H_{il}^d$ is the Hamiltonian of the quadrupolar interaction of the $^7$Li nuclear quadrupole moment $Q$ with the EFG at the Li site, $H_{il}^{contact}$ are the anisotropic dipolar hyperfine coupling and isotropic contact hyperfine to the Mo electron spins, respectively, and the last two terms, $H_{dem}$ and $H^{lor}$, are the bulk demagnetization and Lorentz contributions, respectively [29, 31]. Except for the first term $H_{iz}$ which is for the Zeeman splitting of the $^7$Li nucleus’s spin interaction with $B_0$, all of these terms contribute to the local magnetic and/or electric field at the Li site, as well as to the $^7$Li-NMR spectra, and cause the $^7$Li-NMR frequency shifts.

Among these terms, only $H_{il}^d$ is non-magnetic [29, 30]; under high field limit, $H_{il}^d$ as a perturbed Hamiltonian can cause the $^7$Li-NMR frequency to be shifted from the Larmor frequency, through the interaction of the $^7$Li quadrupole moment $Q$ with the EFG that is created by the crystal lattice (including orbital overlaps and covalence charges) (see section V.D.), and usually can be fully reflected by the $^7$Li-NMR spectrum satellites.

Thus, by measuring the $^7$Li-NMR spectra and observing any potential changes of the spectrum satellites at the direction where the magnetic contributions to the satellites are minimized or zero, we can tell the behavior of the EFG precisely at the atomic scale.

Because the $^7$Li nucleus has a small atomic number $Z = 3$, it is expected [30] that its contact hyperfine couplings to
the Mo electrons ($H_{\text{elec}}^{\text{contact}}$) is negligible. Thus, the system Hamiltonian can be re-written as
\[ H_1 \approx H_{2z} + H_1^0 + H_{\text{le}}^{\text{pp}} + H^{\text{dem}} + H^{\text{lor}}. \]

Here the term $H_1^0$ has a local magnetic field contribution ($B_0$) in the order of $\gamma_2 \mu_2 r^3$, i.e. $B_0 \sim \gamma_2 \mu_2 r^3$, where $\gamma_2$ is the spin moment of the $^7\text{Li}$ nucleus, and $r$ is the distance between neighboring $^7\text{Li}$ nuclei. Considering the value of $\gamma_2 \mu_2 = 7.14h$ (where $h$ is the Planck’s constant) and the minimum value of $r = 3.939\ \text{Å}$ as well as the positions of $^7\text{Li}$ in the crystal lattice, we have a rough estimate on $B_0$, which has an upper limit of $\sim 0.2\ \text{G}$.

Since $B_0$ is independent of temperature and unrelated to the Mo electron spins, it has no contribution to any potential line broadening of the $^7\text{Li}$-NMR spectra. Thus, our interest here is the last three terms, $H_{\text{le}}^{\text{pp}}, H^{\text{dem}},$ and $H^{\text{lor}},$ which are the terms related to the Mo electron spin dynamics and the local magnetic field properties at the Li site. The sources of the purely electronic interaction term $H^{\text{lor}}$ are discussed in the next section.

In section III, we have estimated that at $B_0 = 9\ \text{T}$ at $\theta = +142.5^\circ\ (\theta' = +52.5^\circ),$ $H_{\text{le}}^{\text{pp}}$ contributes to a dipolar field $B_{\text{le}}^{\text{pp}} \approx 0.35\ \text{G}$ at $T \approx 300\ \text{K}$. Now, we can estimate the magnetic field contributions of $H^{\text{dem}}$ and $H^{\text{lor}}$ as [31],
\[ B_{\text{le}}^{\text{pp}} = -4\pi \cdot D \cdot \chi_{\text{de}}(T) \cdot B_0 (N_{\text{Li}} \cdot v_{\text{Mo}}), \]
\[ H^{\text{lor}} = +4\pi/3 \cdot \chi_{\text{de}}(T) \cdot B_0 (N_{\text{Li}} \cdot v_{\text{Mo}}), \]
where $D = 0.35$ is the estimated demagnetization factor at $\theta = +142.5^\circ$ according to the sample size, $N_{\text{Li}}$ is the Avogadro’s number, and $v_{\text{Mo}} = 669.5/24\ \text{Å}^3$ is the unit cell volume per Mo ion. Thus, with $\chi_{\text{de}}(T) \approx 0.4 \times 10^{-4}\ \text{cm}^3\ \text{mol.FU}^{-1}$ (at $T = 300\ \text{K}$) we have [31]
\[ B^{\text{dem}} + B^{\text{lor}} \approx -0.01\ \text{(G)}. \]

Therefore, the dipolar field of the Mo electron spins, i.e. the contribution of Hamiltonian $H_{\text{le}}^{\text{pp}}$ (field $B_{\text{le}}^{\text{pp}}$), is the dominant source of the local magnetic fields at the Li site. $B^{\text{dem}}$ and $B^{\text{lor}}$ together here contribute little to the total local magnetic field at the Li site due to the very small value of $\chi_{\text{de}}$ of the material, i.e. they have negligible impact on the spectra as the temperature varies, as also evidenced by the spectrum versus $T$ data shown in figure 5.

V.D. Theoretical estimation of the $^7\text{Li}$-NMR quadrupolar frequency $\nu_Q$ (EFG)

With the consideration that a nuclear quadrupole moment Q has an antisheielding effect when it interacts with the effective point charge in the ligand lattice and with the valence electrons of the probe atom (the sources of the EFG in general, corresponding to the Hamiltonian $H_{\text{le}}^{\text{pp}}$), equation (4) has a more general form [30]
\[ \nu_Q = (1 - \gamma_e) \frac{eV_0Q}{2\hbar} + (1 - R_0) \frac{eW_0Q}{2\hbar}, \]
where $W_{2z}$ is the principal z-component of the valence EFG, and $\gamma_e$, and $R_0$ are the Sternheimer coefficients (antisheielding factors) of the probe atom, associated with the nuclear quadrupole moment interaction with the effective point charges and the valence electrons in the crystal lattice, respectively [43, 44].

Based on the lattice structure of Li$_{0.9}$Mo$_6$O$_{17}$, we expect the contributions to the EFG at the Li site to come from, 1) the effective charges at all the lattice sites (including the charges at all the Mo and oxygen sites), 2) covalence charges resulting from the virtual charge transport of the electrons from the oxygen 2p-shell to the Li atom 2s-shell, and 3) the orbital overlaps between the Li atom 2s-shell electron with the five surrounding oxygen 2p-shell electrons. Noticeably, the Li electron has an incomplete shell, i.e. the electric charge at the Li nucleus is not spherically symmetric, thus it is reasonable to expect that the Li outer shell (2s) electron has a quadrupole coupling contribution to the EFG at the Li nucleus, which is mainly through the bond covalency with and/or 2s electron orbital overlap with the oxygen 2p electron orbital. Considering that the wave function of the Li 2s electron is spherically symmetric (i.e. independent of the spherical coordinates $\theta$ and $\phi$), we expect that the Li 2s electron orbital overlap with the oxygen 2p electrons to be negligible. Therefore, here we can focus on the contributions of the above terms 1) and 2) only.

From the theoretical relation [29, 30] $V_{2z} = \sum_i k_i q_i (3z_i^2 - r_i^2)/r_i^2$, where $q_i$ is the charge of the ions at each lattice site $i$, $k_i$ is the Coulomb constant, and $r_i$ is the distance from the charges at the $i$th lattice site to the probe nucleus, we estimated straightforwardly the EFG tensor value $V_{2z} = 8.1279 \times 10^{20}\ \text{V m}^{-2}$ at the $^7\text{Li}$ nucleus.

Similarly, from the relation [30] $W_{2z} = -4ke^3/(1r^3)$, where $(1r^3) = 0.38\ \text{Å}^{-3}$ is the expectation value [45, 46] of $1/r^3$ over the covalent orbital. Thus, we have $W_{2z} = 7.296 \times 10^{20}\ \text{V m}^{-2}$.

Besides these, we also have the theoretical value of the antisheilding factor [47] $1 - \gamma_e = 0.75$, and we expect $1 - R_0 = 0.95$ for Li$^{1+}$ as Li has a very small atomic number. Thus, with equation (13) it gives a theoretical value of $\nu_Q = -331.0 + 376.3 = 463.3\ \text{(kHz)}$ for the $^7\text{Li}$ nucleus, which matches well with our measured value $\nu_Q = 44\ \text{kHz}$.

This indicates that the valence contribution to the EFG (or $\nu_Q$) at the Li site has a similar amplitude to that of the ligand lattice.

Furthermore, we can also find that the contribution of the effective charges in the ligand lattice to the EFG (or $\nu_Q$) from the Mo electrons on the average is $\approx 1.5$ times larger than that from the oxygen electrons in magnitude. This is understandable since the Mo electrons have an effective charge $+5.5\ e$
on the average and the oxygen electrons have an effective charge \(-2.0\ e\), while the distances between Li and O and between Li and Mo are rather similar (the later is \(\sim 30\%\) larger).

**VI. Conclusions**

The magnetic dipole field in a single crystal of quasi-one-dimensional (Q1D) paramagnetic conductor Li_{0.9}Mo_9O_{17} is investigated at the atomic scale both theoretically and experimentally, using a paramagnetic electron model and ^7Li-NMR spectroscopy measurements with an externally applied magnetic field \(B_0 = 9\ T\), respectively. The method is described in a general form and the field in the Li_{0.9}Mo_9O_{17} is calculated as a function of the orientation angles \((\theta, \phi)\) of \(B_0\) in space, with experimental observations and demonstrations.

We find that the magnetic dipole field component \(B_{\text{dip}}^0\) parallel to \(B_0\) has no lattice axial symmetry; it is the smallest around the middle between the lattice \(a\) and \(c\) axes, with the central minimum to be 7.5\(^\circ\) closer to the \(a\) than to the \(c\) axis in the \(ac\)-plane, while the maximum of \(B_{\text{dip}}^0\) is at \(\theta = +142.5\(^\circ\), with a maximum value \(\sim 0.35\ G\) when \(B_0 = 9\ T\ \perp\ b\).

By minimizing potential magnetic contributions to the ^7Li-NMR spectrum satellites with the NMR spectroscopy measurements at the direction where the value of the magnetic dipole field is \(\sim 0\) (close to the smallest) (near \(B_0||a\), \(\theta = 90\(^\circ\)\) and \(\phi = 0\(^\circ\)\), the behavior of the electron charge statics is revealed.

Other related important physics quantities such as the spin susceptibility \(\chi_s\), DOS \(D(E_0)\), and the theoretically estimated value of \(\nu_{\text{Q}}\) (EFG) are also discussed.

This investigation demonstrates that the magnetic dipole field from the Mo electrons is the dominant source of the local magnetic fields at the Li site, and there is no signature of change in the value of \(\nu_{\text{Q}}\) (EFG) or in the distribution of it upon cooling in temperature, thus suggesting that the unknown metal—"insulator" crossover at low temperatures is not a charge effect. The work also reveals valuable local electric and magnetic field information for further NMR investigation for a better understanding of the unusual properties of the Q1D material.

**Acknowledgments**

The work was supported by National Natural Science Foundation of China with the grant NO. 61474096 (YZU), US NSF Grant DMR-0334869 (UCLA), and SCA-2012 (UWF). We thank J L Musfeldt, J R Thompson, J J Neumeier and S E Brown for helpful discussions.

**Appendix A. Calculation of the magnetic dipole field at the atomic scale**

The total dipolar field \(\vec{B}\) at the observation site \(P\) is the summation of the field from the moments at all the moment sites \(j\).

\[
\vec{B} \equiv \langle \vec{B}_j \rangle = \sum_j \langle \vec{B}_j \rangle, \tag{A.1}
\]

\[
= \frac{\mu_0}{4\pi} \sum_j \left[ \frac{3 \hat{r}_j (\vec{\mu}_j \cdot \hat{r}_j)}{r_j^5} - \frac{\vec{\mu}_j}{r_j^3} \right], \tag{A.2}
\]

\[
= \frac{\mu_0}{4\pi} \sum_j \left[ \frac{3 \hat{r}_j (\vec{\mu}_j \cdot \hat{r}_j)}{r_j^5} - \frac{(\vec{\mu}_j)}{r_j^3} \right]. \tag{A.3}
\]

The magnetization \(\vec{M}\) due to the electron moments is

\[
\vec{M} = \sum_j (\vec{\mu}_j)/V, \tag{A.4}
\]

where \(V\) is the sample volume.

For paramagnetic electrons, \(\vec{M}\) essentially has a very accurate linear dependence [39] on the externally applied magnetic field \(\vec{B}_0\), i.e.

\[
\vec{M} = \chi H_0, \quad \text{and} \quad H_0 = \vec{B}_0/\mu_0, \tag{A.5}
\]

where \(\vec{H}_0\) is the intensity of the applied magnetic field, and \(\chi\) is the sample paramagnetic susceptibility (isotropic), which can be a \(T\)-dependent variable [the deviation from their linear relation in equation (A.5) is in the order of \(\sim \chi^2 H_0\), which is negligible as \(\chi \sim 10^{-3}\) (cm\(^3\) mol. ion\(^{-1}\)) for most known materials]. If magnetic anisotropy is considered, then

\[
M_i = \chi_i J H_0, \quad \text{where} \quad \chi_i J_i = \partial M_i/\partial H_0, \quad \text{and} \quad \vec{J} = x, y, z.\]

Thus considering equations (A.1)–(A.5), we have

\[
\vec{B} = \frac{1}{4\pi} \chi V \sum_{j=-N}^N \left[ \frac{3 \hat{r}_j (\vec{B}_0 \cdot \hat{r}_j)}{r_j^5} - \frac{\vec{B}_0}{r_j^3} \right], \tag{A.6}
\]

where \(N\) in the index \(j\) is the number of sites for the electron moments. Here the temperature dependence of \(\vec{B}(T)\) is determined by the value of \(\chi(T)\). Since our consideration is for the magnetic dipole field from the spins of the conduction electrons, it is the Pauli spin susceptibility \(\chi_s(T)\) that should be used for our dipolar field calculation.

The orientation of the applied magnetic field \(\vec{B}_0\) can be expressed as

\[
\vec{B}_0 = B_{0\alpha} \hat{e}_\alpha + B_{0\beta} \hat{e}_\beta + B_{0\gamma} \hat{e}_\gamma = B_0 (\sin \theta \cos \phi \hat{i} + \sin \theta \sin \phi \hat{j} + \cos \theta \hat{k}) \text{, where} \theta \text{ and} \phi \text{ are the standard spherical angles in the Cartesian system} [42], \text{as shown in figure 1(b).}

The calculation using equation (A.6) requires Cartesian system that can always be made, where \(xz\)-plane is chosen to be placed in the \(ac\)-plane and the \(z\)-axis is along the \(c\)-axis, as illustrated in figure 1(c), from which we have

\[
\begin{align*}
\hat{e}_x &= e_{0x} = \cos \theta \cos \phi, \\
\hat{e}_y &= e_{0y} = \cos \theta \sin \phi, \\
\hat{e}_z &= e_{0z} = \sin \theta.
\end{align*}
\]
where $\alpha$, $\beta$, and $\gamma$ are the lattice constants (including the values of $a$, $b$, and $c$), $x'_0$, $y'_0$, and $z'_0$ are the atom coordinates in the lattice $abc$-coordinate system, $\bar{e}_a$, $\bar{e}_b$, and $\bar{e}_c$ are the expression for the unit vectors of the $a$, $b$, and $c$ axes of the crystal lattice in the lattice coordinate system, respectively, and $\bar{e}_x$, $\bar{e}_y$, and $\bar{e}_z$ are the unit vectors of the Cartesian $x$, $y$, and $z$ axes, respectively. Thus with equation (A.7) the coordinates between the lattice and Cartesian coordinate systems are conveniently transformable.

The crystal lattice [14, 17] of Li$_{0.9}$Mo$_6$O$_{17}$ has a monoclinic crystal group $P2_1/n$, which has four equivalent sites in total for each site due to the symmetry of its 2-fold screw axis (b is the default axis for the rotation). The space group also has an axis of a mirror plane, which is $\perp b$, and the four equivalent sites are

$$(x', y', z')$$

$$(-x', 1/2 + y', -z')$$

$$(-x', -y', z')$$

$$(x', 1/2 - y', z'),$$

i.e. each of which has the rest of three other equivalent sites to it. Here $x'$, $y'$, and $z'$ are the fractional coordinates in the lattice $abc$-system, and their relation with $x'_0$, $y'_0$, and $z'_0$ in equation (A.7) is, $x'_0 = ax'$, $y'_0 = by'$, and $z'_0 = cz'$, respectively.

In each unit cell of Li$_{0.9}$Mo$_6$O$_{17}$, there are six independent Mo sites, Mo1, Mo2, ..., Mo6, where the paramagnetic dipole moments (conduction electrons) are from, and there is only one independent Li site. Thus, considering that each site has other three structurally equivalent sites from the lattice symmetry, in total we have 24 ($6 \times 4$) Mo sites and 4 Li sites in each unit cell. Apparently, all the 24 Mo sites (each of them has a magnetic dipole moment) contribute to the dipolar fields at the Li sites, while the fields at each Li site are the same.

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