# Quadrupole Interactions of Muonium in Crystals *

V. G. Baryshevskii, S. A. Kuten, and V. I. Rapoport
Department of Physics, Byelorussian V. I. Lenin State University, Minsk, USSR

Z. Naturforsch. **41 a,** 19–23 (1986); received August 5, 1985

The properties of muonium having an electric quadrupole moment in crystals are briefly reviewed. A detailed analysis of the experimental situation in $\alpha$-quartz is given, since the $\alpha$-$SiO_2$ lattice is a place of localization of not only muonium, but also of hydrogen and deuterium atoms. The temperature and isotopic dependences of the experimentally determined parameters of the quadrupole interaction of hydrogen, deuterium and muonium, as well as the nature of their trapping sites in the $\alpha$-quartz lattice are discussed. It is shown that the change of the quadrupole interaction strength and symmetry with temperature is caused by the diffusion of muonium. It is mentioned that a significant role in explaining the isotopic dependence is played by the zero-point vibrations of the hydrogen-like atom localized in the lattice.

## 1. Introduction

At present, in studies of materials the so-called $\mu^+$SR technique [1] is extensively applied, in which various parameters of the physical and chemical processes occurring in the material are determined by the behaviour of the positive muon ($\mu^+$) spin polarization. The high sensitivity of the $\mu^+$ to the local magnetic field variations leads to its use mainly as a magnetic probe in solids. In addition, the $\mu^+$ can serve as an electric probe. Indeed, the positive $\mu^+$ thermalized in matter can form a muonium atom ($\mathrm{Mu} \equiv \mu^+ e^-$). Mu is a light isotope of a hydrogen (H), whose nucleus $\mu^+$ does not have an electric quadrupole moment ($Q$). However, the atom as a whole even in the ground state has $Q$ comparable in its value with the nuclear quadrupole moments [2]. The fact that Mu has $Q \neq 0$ makes it possible to carry out numerous studies with $\mu^+$ similar to investigations performed in the NQR spectroscopy, thereby obtaining information on the distribution of inhomogeneous electric fields in matter. However, contrary to the situation in NQR spectroscopy, where the nuclear quadrupole moment is fully determined by the intranuclear processes and is not affected by the environment of the nucleus, the interaction of Mu with its environment may considerably modify the Mu state in the solid compared to its vacuum state. The so-called anomalous muonium found in semiconductors [3] can be given as an example. It is evident that in the case of a strong interaction between Mu and host atoms the interpretation of experimental data in terms of a quadrupole interaction (QI) of Mu with the lattice will not be satisfactory. As for the cases when Mu experiences very little interaction with the host atoms, it seems most natural to take into account only the interaction of the $Q$ of muonium with the crystalline field.

The QI of muonium has so far been discovered only in monocrystals of $\alpha$-$SiO_2$ [4–9], $H_2O$ and $D_2O$ [10]. In the present paper a detailed analysis of the experimental situation in $\alpha$-quartz is given, since the $\alpha$-$SiO_2$ lattice is a place of localization of not only Mu, but also of hydrogen and deuterium (D) atoms [11].

## 2. Quadrupole Splitting of Hydrogen-Like Atom Levels in Crystals

The spin-Hamiltonian describing a hydrogen-like atom with $Q$ is given by

$$\mathscr{H} = A\boldsymbol{S}\boldsymbol{I} + \tfrac{1}{6} Q_{ik}\,\varphi^0_{ik}\,, \tag{1}$$

where the first term is the standard hyperfine interaction (HFI) between the nuclear spin $\boldsymbol{I}$ and the electron spin $\boldsymbol{S}$, and the second one is the QI of the atom. In (1) $A$ is the HFI constant of the atom, $\varphi^0_{ik}$ is the tensor of the electric field gradient (EFG) at the atom centre and $Q_{ik}$ is the quadrupole moment tensor of the atom.

---

* Communicated to the VIIIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Darmstadt, July 22–26, 1985.

Reprint requests to Prof. V. G. Baryshevskii, Department of Physics, Byelorussian V. I. Lenin State University, Minsk 220080, USSR.

0340-4811 / 86 / 0100-0019 $ 01.30/0. – Please order a reprint rather than making your own copy.

It has been shown in [12] that the spin-Hamiltonian (1) in the case of $I = 1/2$ is mathematically identical with the phenomenological anisotropic HFI of the type

$$\mathscr{H} = A_{ik}\, S_i\, I_k\,, \tag{2}$$

and that the phenomenological constants $A_{ii}$ and the microscopic characteristics of the atomic HFI and QI are described by relations of the form

$$\begin{aligned} A &= (A_{xx} + A_{yy} + A_{zz})/3, \\ d &= (2A_{zz} - A_{xx} - A_{yy})/3, \\ \eta &= |3(A_{xx} - A_{yy})/(2A_{zz} - A_{xx} - A_{yy})|\,. \end{aligned} \tag{3}$$

Here $d = eQ\,\varphi^0_{zz}$ is the QI constant, $0 \leqq \eta = |(\varphi^0_{xx} - \varphi^0_{yy})/\varphi^0_{zz}| < 1$ is the asymmetry parameter of the EFG tensor, and $e$ is the electron charge.

It can similarly be shown that the spin-Hamiltonian (1) in the case of $I = 1$ is equivalent to a spin-Hamiltonian of the type

$$\mathscr{H} = A_{ik}\, S_i\, I_k + \frac{e\,Q\,\varphi^0_{ik}}{12}\,(I_i\, I_k + I_k\, I_i - \tfrac{2}{3}\,\boldsymbol{I}^2\,\delta_{ik})\,, \tag{4}$$

where $A_{ik} = A\,\delta_{ik} + e\,Q\,\varphi^0_{ik}/3$ and $\delta_{ik}$ is the Kronecker symbol. Hence, if $I = 1$,

$$\begin{aligned} A &= (A_{xx} + A_{yy} + A_{zz})/3\,, \\ d &= 2A_{zz} - A_{xx} - A_{yy}\,, \\ \eta &= |3(A_{xx} - A_{yy})/(2A_{zz} - A_{xx} - A_{yy})|\,. \end{aligned} \tag{5}$$

Generally speaking (1) and (3)–(5) are valid for a "point" atom. At a first glance this approach is justified, since the atomic size in matter can be relatively small (less than the characteristic interatomic distances). However, the influence of this size may still prove to be important, since the characteristic distances of the quadrupole moment density distribution can be rather extended and comparable with the interatomic distances. According to [13], (1) and (3)–(5) remain valid also in the case of a "non-point" atom but a so-called "generalized" EFG tensor $\varphi_{ik}$ must be substituted for $\varphi^0_{ik}$:

$$\varphi_{ik}(\boldsymbol{R}) = \varphi^0_{ik}(\boldsymbol{R}) + \Delta_{ik}(\boldsymbol{R})\,. \tag{6}$$

Here the first term is the EFG tensor at the site of the atomic centre of mass ($\varphi^0_{ii}(\boldsymbol{R}) = -4\pi\,\varrho(\boldsymbol{R})$, where $\varrho(\boldsymbol{R})$ is the charge density at point $\boldsymbol{R}$). The value $\Delta_{ik}(\boldsymbol{R})$ is caused by the "finite size" of the atom. Moreover, the parameters $A$, $d$ and $\eta$ turn out to be averaged due to the vibrations of the atomic centre of mass [13], and these parameters should be considered as certain constants effective for a given material. The experimental determination of these constants presents considerable interest.

## 3. Muonium, Hydrogen and Deuterium in α-Quartz

The quadrupole moment of Mu in matter was first discovered by $\mu^+$SR experiments [4] in α-quartz. Experimental results concerning the QI of Mu in the α-$SiO_2$ lattice are published in [4–9]. It is established that at low temperatures $T < 120$ K, Mu in α-quartz is described by a completely anisotropic HFI of the type (2) [6, 7]. H in α-$SiO_2$ is characterized by a spin-Hamiltonian of the same type. In addition, at $T < 120$ K α-quartz can be a place of localization of D, described as follows [11]:

$$\mathscr{H} = A_{ik}\, S_i\, I_k + \tfrac{1}{6}\, Q^{\mathrm{d}}_{ik}\, \varphi^{\mathrm{d}}_{ik}\,, \tag{7}$$

where the second term is the QI of the deuteron. Expressions (4) and (7) are equivalent if ($\varphi^0_{ik} \to \varphi_{ik}$)

$$Q^{\mathrm{d}}\, \varphi^{\mathrm{d}}_{ik} = \tfrac{1}{3}\, Q\, \varphi_{ik}\,, \tag{8}$$

where $Q^{\mathrm{d}}$ is the quadrupole moment of the deuteron.

Unfortunately, the EPR experiments [11] did not give any reliable information about the $\varphi^{\mathrm{d}}_{ik}$ tensor; therefore it is not possible to check the validity of (8). As for the $A_{ik}$ matrix, its determination is quite reliable. The same experiments helped to determine the $A_{ik}$ matrix for H, whereas the phenomenological constants $A_{ii}$ for Mu were obtained in [7]. It should be noted that the experiments [6, 7] did not reveal the angles of the principal axes of the $A_{ik}$ matrix with respect to the α-$SiO_2$ crystal axes.

With the constants $A_{ii}$ known, one can calculate the parameters $A$, $d$ and $\eta$ using the relations (3), (5). The results of these calculations are given in the Table 1.

It can be seen from Table 1 that the parameter $\eta$ is practically the same for Mu, H and D within the accuracy of measurements. This proves that the hydrogen isotopes at low $T$ occupy the same sites in α-$SiO_2$. This conclusion agrees with the conclusions of [6, 11, 13]. Furthermore, for all three isotopes the HFI constant $A$ is larger than the vacuum value $A_{\mathrm{vac}}$, the ratio $A/A_{\mathrm{vac}}$ increasing with increasing atomic mass. The temperature dependence should be

Table 1. The constants $A$, $d$ and $\eta$ for the hydrogen isotopes in $\alpha$-quartz.

| Isotope | Temp. (K) | $A$ (MHz) | $d$ (MHz) | $\eta$ | $A/A_{\mathrm{vac}}$ |
|---|---|---|---|---|---|
| Mu | 30 | 4505.0(5) | 9.44(3) | 0.367(5) | 1.00934(11) |
| H | 40 | 1451.73(3) | 4.36(4) | 0.330(19) | 1.02205(2) |
|  | 80 | 1451.65(4) | 4.19(6) | 0.349(26) | 1.02200(3) |
|  | 100 | 1451.38(2) | 4.18(3) | 0.352(14) | 1.02181(1) |
| D | 40 | 223.46(2) | 2.15(10) | 0.240(67) | 1.02375(9) |
|  | 100 | 223.40(2) | 1.99(8) | 0.289(72) | 1.02357(9) |

analysed separately, but here we should only point out that the observed slight decrease of $A$ with increasing $T$ in $\alpha$-$SiO_2$ (this is also true for Mu, since at $T = 296$ K, $A \approx 4496$ MHz [7]) is consistent with the temperature dependence of $A$ for Mu and H in KCl [14, 15] and H and D in $CaF_2$ [16], but is quite opposite to the case of Mu in $CaF_2$ [15].

Since the hydrogen isotopes in $\alpha$-quartz are in a vacuum like state, it is interesting to compare the ratio of the QI constants with the ratio of the magnetic moments of the corresponding nuclei. (According to [2], in vacuum $Q_i/Q_j \approx \mu_i/\mu_j$, where $Q_i$ is the quadrupole moment of the $i$-th atom and $\mu_i$ is the magnetic moment of its nucleus.) Using the $d$ values from the Table 1 one finds $d_{\mathrm{Mu}}/d_{\mathrm{H}} \approx 0.68\, \mu_\mu/\mu_{\mathrm{p}}$, $d_{\mathrm{H}}/d_{\mathrm{D}} \approx 0.62\, \mu_{\mathrm{p}}/\mu_{\mathrm{d}}$ and $d_{\mathrm{Mu}}/d_{\mathrm{D}} \approx 0.42\, \mu_\mu/\mu_{\mathrm{d}}$. Thus there is a considerable difference between $d_i/d_j$ and the expected value of $\mu_i/\mu_j$ in $\alpha$-$SiO_2$, the ratio $d_i\, \mu_j/d_j\, \mu_i$ decreasing with the increasing difference between the masses of the heavier ($j$) and lighter ($i$) isotope. The considerable difference between $d_i\, \mu_j/d_j\, \mu_i$ and 1 may be connected with both the existence of a considerable lattice-induced $Q$ of the atom (the estimations are given in [17]) and the presence of a relatively large EFG tensor correction $\Delta_{ik}$. Nothing more definite can be said about it so far. As for the observed mass dependence, it indicates the important role of the zero-point vibrations of the hydrogen-like atom about its equilibrium position in the lattice.

Let us estimate the influence of the zero-point vibrations on the HFI constant of a hydrogen-like atom with mass $M$. For this purpose we assume a specific type of the electric charge distribution. Let the electrostatic potential $\varphi(\boldsymbol{R})$ at the impurity atom be induced by the $N$ nearest neighbour host atoms having the nuclear charges $+ Z_i\, e$ and being located at points $\boldsymbol{r}_i$, the potential induced by each host atom being a screened Coulomb potential:

$$\varphi(\boldsymbol{R}) = \sum_{i=1}^{N} Z_i\, e\, \frac{\exp[-\varkappa_i |\boldsymbol{R} - \boldsymbol{r}_i|]}{|\boldsymbol{R} - \boldsymbol{r}_i|}, \tag{9}$$

where $\varkappa_i^{-1}$ is the screening parameter for the $i$-th host atom. In this case, simple though awkward calculations result in the expression

$$A = A_{\mathrm{vac}}(1 + \Delta), \tag{10}$$

where

$$\begin{aligned}\Delta = \frac{11}{12}\, a_0^3\, \frac{m_{\mathrm{n}} - m_{\mathrm{e}}}{m_{\mathrm{n}} + m_{\mathrm{e}}} \cdot \sum_{i=1}^{N} \frac{Z_i\, \varkappa_i^2}{r_{\mathrm{i}}} \exp\left[\left(\frac{\varkappa_i}{2\alpha}\right)^2\right] \\ \cdot \left[2\, \mathrm{sh}\,(\varkappa_i\, r_{\mathrm{i}}) + \exp(-\varkappa_i\, r_i) \cdot \mathrm{erf}\left(\frac{\varkappa_i}{2\alpha} - \alpha\, r_i\right)\right. \\ \left. - \exp(\varkappa_i\, r_i) \cdot \mathrm{erf}\left(\frac{\varkappa_i}{2\alpha} + \alpha\, r_i\right)\right].\end{aligned} \tag{11}$$

In obtaining (10) and (11), averaging over the ground state of the harmonic oscillator was carried out. In (11) $m_{\mathrm{e}}$ and $m_{\mathrm{n}}$ are the masses of electron and nucleus, respectively, $\alpha^2 = M\omega$, $\omega \sim M^{-1/2}$ is the cyclic frequency of the zero-point vibrations, $a_0$ is the Bohr radius and $\mathrm{sh}\,(Z)$ is the hyperbolic sine.

The value $\Delta$ may be positive or negative. For example, if $\varkappa_i/2\alpha \gg \alpha\, r_i$, then $\Delta > 0$ and $\Delta \sim \sqrt[4]{M}$. Such a mass dependence of $\Delta$ makes it possible to qualitatively explain the behaviour of $A$ for a hydrogen-like atom not only in $\alpha$-$SiO_2$, but also in NaF [18, 19], in $CaF_2$ [15, 16], in $SrF_2$ [20], and in the condensed phase of Ar [21], since while using the model potential (9) we did not specify the kind of crystal. But if $\varkappa_i/2\alpha \ll \alpha\, r_i$, then $\Delta < 0$ and $\Delta \sim \exp(\mathrm{const}/\sqrt{M})$. This implies that in the case of $A < A_{\mathrm{vac}}$ the ratio $A/A_{\mathrm{vac}}$ also increases with the atomic mass. This mass dependence of $A$ explains in its turn the behaviour of a hydrogen-like atom in alkali halides [14, 15, 19]. Thus (11) qualitatively explains both the increase and the decrease of the HFI constant $A$ for the hydrogen-like atom in a crystal compared to the vacuum value $A_{\mathrm{vac}}$, as well as the increase of the ratio $A/A_{\mathrm{vac}}$ with the atomic mass. It should be pointed out that to obtain quantitative estimates it is probably necessary to use more realistic potentials.

## 4. Diffusion of Muonium in $\alpha$-Quartz

In the temperature region $T > 200$ K the HFI of Mu in $\alpha$-quartz becomes axially symmetric (the axis of symmetry is the three-fold screw axis $\hat{c}$ of quartz) [4, 5, 7, 8]. Moreover, the QI constant $d$ decreases and changes its sign. According to [8], e.g., $d = -0.517(8)$ MHz at $T = 293$ K. It is quite natural to relate the observable decrease of the absolute value of the QI constant with increasing temperature to the diffusion of Mu in $\alpha$-$SiO_2$. However, it is still not clear how to account for the fact that the sign of $d$ changes with temperature: whether the high temperature case is fully determined by the diffusion or if there are in addition some qualitative modifications in the Mu wave function. To answer this question one should primarily know the orientation of the tensor $\varphi_{ik}$ principal axes for Mu in $\alpha$-quartz at low tempoeratures. In the recent $\mu^+$SR experiments [9] this orientation was determined and it was confirmed that at low temperatures Mu occupies the same sites in $\alpha$-$SiO_2$ as H(D). According to [9], for Mu in $\alpha$-$SiO_2$ at $T = 75-120$ K the EFG tensor principal axes are oriented in the following way: the $\hat{x}$-axis is perpendicular to the two-fold crystal axis $\hat{a}$ and makes an angle $\alpha_0 = (27 \pm 2)°$ with the $\hat{c}$-axis (for H and D $\alpha_0 \approx 24°$ [11]), the $\hat{y}$-axis is collinear with the $\hat{a}$-axis and the $\hat{z}$- and $\hat{c}$-axis make an angle $90° - \alpha_0$.

Now let us show that the observed change of the strength and symmetry of the muonium QI in $\alpha$-quartz with $T$ is caused by the fast diffusion of Mu through the lattice.

Since there are three equivalent two-fold axes $\hat{a}$ in the $\alpha$-$SiO_2$ lattice there should exist three equivalent Mu sites associated with these axes [7, 11]. If the frequency $1/\tau$, with which Mu jumps from one site to the next, is much larger than $d$, then the behaviour of Mu is determined by the averaged spin-Hamiltonian (1) [22]. When Mu is moving from one site to another the EFG tensor principal axes "rotate" about the $\hat{c}$-axis in such a way that the angle $\alpha_0$ remains fixed. Therefore the averaging of the spin-Hamiltonian with respect to the angles leads to the fact that the average EFG, experienced by the fast jumping Mu has an axial symmetry relative to the $\hat{c}$-axis; as regards the observed QI constant, $\bar{d}$ it will be expressed as follows:

$$\bar{d} = [\sin^2 \alpha_0 - \tfrac{1}{2} \cos^2 \alpha_0 (1 - \eta)]\, d. \qquad (12)$$

Substituting in (12) $\alpha_0 = (27 \pm 2)°$, $\eta = 0.353(4)$, $= 9.27(2)$ MHz [9], we obtain $\bar{d} = -0.05(4)\, d = -0.46(37)$ MHz. Since a complete correspondence with the experimentally measured value $d = -0.517(8)$ MHz is evident, it can be asserted that the high temperature case is fully determined by the fast hopping motion of Mu between its low temperature sites in the $\alpha$-$SiO_2$ lattice and is not related to any qualitative modifications of the muonium wave function.

In conclusion it should be pointed out that it would be of great interest to study the temperature dependences $d(T)$ and $\eta(T)$ in the temperature region $120-200$ K. The experimental investigations in this temperature region would help to clarify the question how the transition to a fast diffusion is realized, i.e. whether there is a slow diffusion of Mu through the $\alpha$-quartz lattice.

[1] J. H. Brewer and K. M. Crowe, Ann. Rev. Nucl. Part. Science **28,** 239 (1978).

[2] V. G. Baryshevskii, Nuclear Optics of Polarized Media, Byelorussian State University Press, Minsk 1976; V. G. Baryshevskii and S. A. Kuten, Phys. Letters **67 A,** 355 (1978).

[3] E. Holzschuh, W. Kündig, P. F. Meier, B. D. Patterson, J. P. F. Sellschop, M. C. Stemmet, and H. Appel, Phys. Rev. **A 25,** 1272 (1982).

[4] J. H. Brewer and D. P. Spencer, Hyperfine Inter. **6,** 181 (1979); J. H. Brewer, D. S. Beder, and D. P. Spencer, Phys. Rev. Lett. **42,** 808 (1979).

[5] J. A. Brown, S. A. Dodds, T. L. Estle, R. H. Heffner, M. Leon, and D. A. Vanderwater, Solid State Commun. **33,** 613 (1980).

[6] J. H. Brewer, D. P. Spencer, D. G. Fleming, and J. A. R. Coope, Hyperfine Inter. **8,** 405 (1981).

[7] E. Holzschuh, W. Kündig, and B. D. Patterson, Helv. Phys. Acta **54,** 552 (1981).

[8] S. G. Barsov, V. G. Baryshevskii, A. L. Getalov, V. A. Gordeev, S. P. Kruglov, S. A. Kuten, L. A. Kuzmin, S. M. Mikirtychyants, and G. V. Shcherbakov, Pis'ma v Zh. Eksp. Teor. Fiz. **39,** 278 (1984).

[9] S. G. Barsov, A. L. Getalov, V. A. Gordeev, S. P. Kruglov, L. A. Kuzmin, S. M. Mikirtychyants, G. V. Shcherbakov, V. G. Baryshevskii, S. A. Kuten, and V. I. Rapoport, Phys. Letters A (1985) (to be published).

[10] P. W. Percival, J.-C. Brodovitch, S.-K. Leung, and K. E. Newman, Hyperfine Inter. **17–19,** 543 (1984).

[11] J. Isoya, J. A. Weil, and P. H. Davis, J. Phys. Chem. Sol. **44,** 335 (1983).

[12] V. G. Baryshevskii, S. A. Kuten, and V. I. Rapoport, Phys. Letters **88 A,** 289 (1982).

[13] V. G. Baryshevskii, S. A. Kuten, and V. I. Rapoport, J. Phys. **C 16,** 6651 (1983).
[14] G. Heder, J. R. Niclas, and J. M. Spaeth, phys. stat. solidi (b) **100,** 567 (1980).
[15] R. F. Kiefl, E. Holzschuh, H. Keller, W. Kündig, P. F. Meier, B. D. Patterson, J. W. Schneider, K. W. Blazey, S. L. Rudaz, and A. B. Denison, Phys. Rev. Lett. **53,** 90 (1984).
[16] S. G. Sligar and H. Blum, Phys. Rev. **B 3,** 3587 (1971).
[17] J. A. Weil. Canad. J. Phys. **59,** 841 (1981).
[18] Chr. Hoentzsch and J. M. Spaeth, Solid State Commun. **29,** 577 (1979).
[19] H. P. Baumeler, K. W. Blazey, W. J. Choyke, T. L. Estle, H. Keller, R. F. Kiefl, W. Kündig, P. F. Meier, W. Odermatt, B. D. Patterson, S. L. Rudaz, J. W. Schneider, and C. Schwab, SIN Newsletter **17,** 69 (1985).
[20] R. G. Bessent, W. Hayes, J. W. Hodby, P. H. S. Smith, J. H. Beaumont, and H. F. Macdonald, Proc. Roy. Soc. London **A 309,** 69 (1969).
[21] S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, J. Chem. Phys. **32,** 963 (1960); R. F. Kiefl, J. B. Warren, G. M. Marshall, C. J. Oram, and C. W. Clawson, J. Chem. Phys. **74,** 308 (1981).
[22] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford 1961.