Mössbauer Spectroscopic Evidence of Angle-Dependent Intersystem Crossing in $LiNbO_3:Fe^{3+}$

R. Doerfler,(1) W. Gruber,(1) P. Gütlich,(3) K. M. Hasselbach,(3) O. Leupold,(1) B. Molnár,(2)
D. L. Nagy,(1),(2) G. Ritter,(1) H. Spiering,(3) and F. Tuczek(3)
(1)*Physikalisches Institut, Universität Erlangen-Nürnberg, D-8520 Erlangen, Federal Republic of Germany*
(2)*Central Research Institute for Physics, H-1525 Budapest, Hungary*
(3)*Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, D-6500 Mainz, Federal Republic of Germany*

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Mössbauer emission spectra of $LiNbO_3:^{57}Co$ single crystals in magnetic fields up to 5 T at 4.2 K show initial populations of the $^6A_{1g}$ Zeeman substates of Fe^{3+} which depend strongly on the angle between the crystallographic c axis and the magnetic field. This is interpreted in terms of a crystal-field effect on excited states which influences the initial populations of the Zeeman sublevels of the $^6A_{1g}$ ground term after the electron-capture decay of ^{57}Co. An intersystem crossing process due to orbit-lattice interaction can fairly well explain the angular dependence.

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Aftereffects of the nuclear decay leading to a Mössbauer transition often result in anomalous states of the daughter atom. The properties of these states can be studied in Mössbauer-emission experiments, if their lifetime is longer than or comparable to the nuclear lifetime. The transient electronic states preceding the Mössbauer transition remained, up till now, hidden from further analysis.

The observation of long-lived low-energy electronic excitations after the electron capture (EC) of ^{57}Co in $ZnS:^{57}Co$,[1] in frozen aqueous solution of $^{57}CoCl_2$,[2] and in $LiNbO_3:^{57}Co$[3] offers a possibility to obtain information about transient states even if they cannot directly be observed.

In the above case several electronic substates split by the crystal electric field (CEF)[1] or by an external magnetic field[2,3] have been observed simultaneously. The analysis of their average populations during the decay of the Mössbauer level showed[1,3] that their nonequilibrium populations (i.e., the populations at ca. 10^{-8} s after the EC) are probably determined by the properties of higher-lying transient electronic states. In earlier works[4,5] a uniform initial population has been suggested in similar systems. In this Letter direct evidence will be presented for the role of transient states in the initial population of the $^6A_{1g}$ Zeeman sublevels of the nucleogenic Fe^{3+} ions in $LiNbO_3:^{57}Co$ single crystals.

A small plate of high-purity $LiNbO_3$ single crystal with the c axis perpendicular to the sample plane has been doped with ca. 110 MBq (3 mCi) of ^{57}Co by the method described earlier.[3] Mössbauer spectra have been measured at 4.2 K in longitudinal magnetic fields up to $B=5$ T with use of a single-line absorber of $Na_4[Fe(CN)_6]\cdot 10H_2O$ containing 0.25 mg/cm² ^{57}Fe. The angle θ between the c axis and the magnetic field could be varied from 0° to 70°. The 7% stray field at the absorber has been taken into account in the evaluation.[3] Figure 1 shows the spectra at $B=4$ T at different

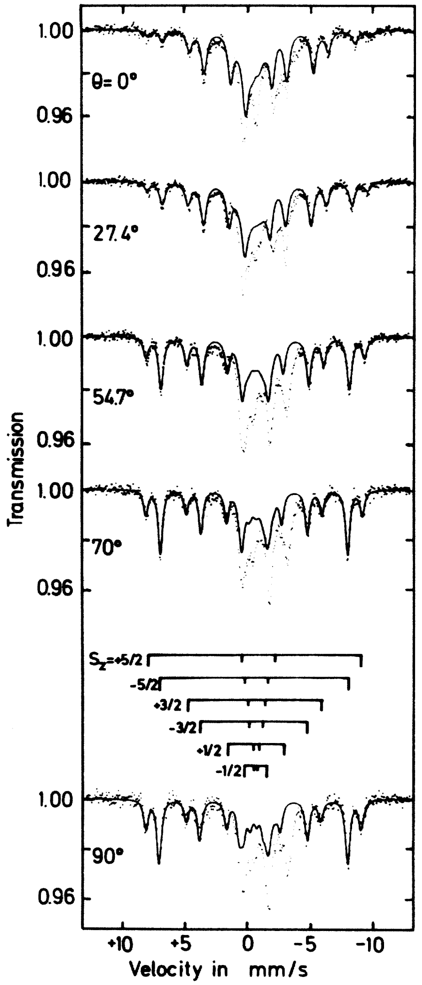

FIG. 1. Mössbauer emission spectra of $LiNbO_3$ single crystals at 4.2 K in a longitudinal magnetic field of 4 T at various angles between the magnetic field and the crystallographic c axis. The full line is the fit of the Fe^{3+} fraction. The contributions of the six electronic substates are indicated for the $\theta=90°$ spectrum.

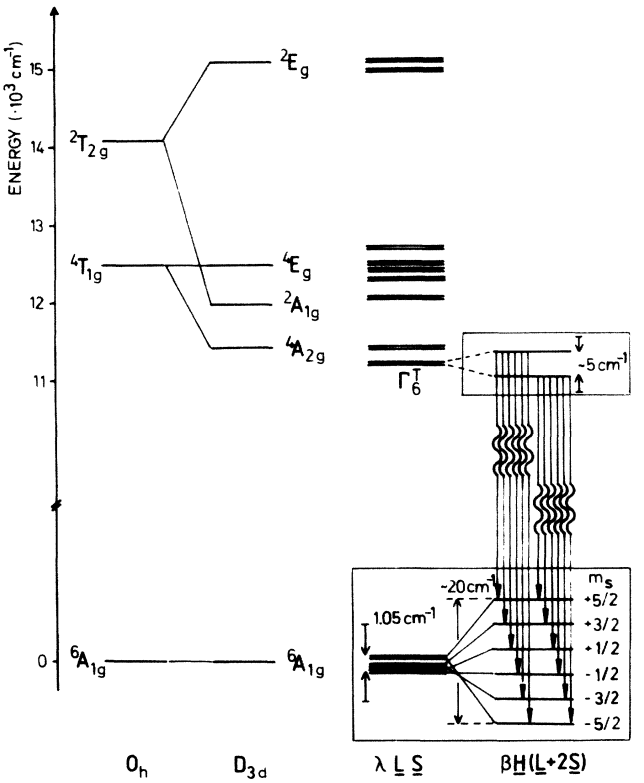

FIG. 2. The low-lying electronic levels of Fe^{3+} in octahedral field, in trigonal field, with spin-orbit coupling, and with magnetic field (4 T). The radiationless transitions which are considered in the text are indicated by wavy lines.

angles θ (the $\theta = 90°$ spectrum stems from another sample with its c axis in the sample plane[3]). Obviously, the relative line intensities of the Fe(III) contribution strongly depend on θ. In the central part of the spectrum the Fe(III) lines overlap with an Fe(II) fraction making it difficult to determine the intensities of all m_s subspectra. However, as fast relaxation within the $^5T_{2g}$ ground state of Fe(II) gives no rise to aftereffects, the Fe(II) part of the emission spectrum can be compared to the corresponding absorption spectrum. Therefore, after subtraction of the well-defined $m_s = \pm\frac{5}{2}$, $\pm\frac{3}{2}$, and $+\frac{1}{2}$ Zeeman subspectra from the total emission spectrum at $\theta = 90°$ and $B = 4$ T, the intensity of the remaining $m_s = -\frac{1}{2}$ subspectrum can be determined such that the Fe(II) fraction reproduces the shape of the corresponding absorption spectrum.[3] In this way an Fe(III) fraction of the total area of 0.66 ± 0.05 was obtained. In the following, only the angular dependence of the summed-up intensities $I_{+m_s} + I_{-m_s}$, $m_s = \frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$, is considered. As the $m_s = \pm\frac{5}{2}$ and $\pm\frac{3}{2}$ subspectra are unaffected by the Fe(II) fraction at all angles, $I_{+1/2} + I_{-1/2}$ can be determined by the total area of the spectrum and the known Fe(III) fraction. The angular dependence of the intensities $I_{m_s} + I_{-m_s}$ can be reasonably well described by the empirical expression

$$I_{m_s}(\theta) + I_{-m_s}(\theta) = \tfrac{1}{3} + \alpha_{m_s}(3\cos^2\theta - 1)/2, \qquad (1)$$

with $\alpha_{5/2} = -0.22$, $\alpha_{3/2} = 0.05$, and $\alpha_{1/2} = 0.17$.

The observed θ dependence of an Fe^{3+} Mössbauer spectrum is rather surprising, because the zero-field splitting in the ground state is only about $\frac{1}{20}$ of the Zeeman splitting at 4 T.[6] In contrast to this, all nonground terms of the $3d^5$ high-spin Fe^{3+} ion are non-S terms having CEF splittings larger by 1 or 2 orders of magnitude than the Zeeman splitting.[7] When the crystal is rotated the $^6A_{1g}$ wave functions are essentially fixed to the magnetic field while all excited-term wave functions are essentially fixed to the crystal because of the presence of orbital momentum. Therefore, the transition matrix elements between any nonground term and the $^6A_{1g}$ term should depend on θ. The initial population of the m_s sublevels is proportional to I_{m_s} since any significant relaxation ($\tau_r \lesssim 10^6$ s) within the $^6A_{1g}$ term at 4.2 K can be ruled out.[8]

The EC decay of the ^{57}Co nucleus and the following Auger cascade presumably result in an excitation of practically all electronic levels of the nucleogenic Fe^{3+} ion. These excited states relax to thermal equilibrium by various processes; we assume that the rate-determining step is the transition from the lowest excited Kramers doublet, lying at ca. 11 000 cm^{-1} above the ground state, to the $^6A_{1g}$ manifold (cf. Fig. 2). The ground state is the only spin sextet occurring within the d^5 configuration. Thus, relaxation to the ground manifold is always spin forbidden whereas relaxation among the excited states may proceed either by internal conversion ($\Delta S = 0$) or intersystem crossing ($\Delta S \neq 0$). Concerning the latter process the relative decay rates depend on the strength of spin-orbit coupling, which in turn is higher between two energetically close excited levels than between any excited level and the ground state.

Consequently, it can be assumed that the lowest excited Kramers doublet is populated prior to the final transition to the $^6A_{1g}$ ground state. This doublet transforms according to Γ_6^T of the double trigonal group[9] (see below). The initial population P_k^0 of a ground-state sublevel k is thus entirely determined by the relative transition probabilities w_{jk} from the excited sublevels j belonging to Γ_6^T weighted by the populations P_j of those states. We assume further that the transitions $j \rightarrow k$ proceed radiationless and that only the electronic part of the transition operator determines the angular dependence of the anomalous ground-state populations.

If we adopt the orbit-lattice interaction formalism originally applied by Blume and Orbach to the case of relaxation within the ground manifold[10] to our intersystem crossing process and evaluate only electronic matrix elements, the initial populations P_k^0 are then given by

$$P_k^0 \sim \textstyle\sum_j P_j \sum_i \sum_n \left| \displaystyle\sum_{l=2,4} V(\Gamma_{ig}, l) \langle j | C(\Gamma_{ig}, l, n) | k \rangle \right|^2. \qquad (2)$$

Γ_{ig} denote the irreducible representations E_g and T_{2g} of the group O_h, according to which the normal vibrations of the molecular cluster can be classified (the A_{1g} vibration has been omitted on the assumption that the transition proceeds "vertically," i.e., without change along the totally symmetric nuclear coordinate). $C(\Gamma_{ig},l,n)$ are linear combinations of spherical harmonics adapted to O_h symmetry where n denotes a component of the representation Γ_{ig} of O_h and the constants $V(\Gamma_{ig},l)$ are expansion coefficients of the dynamic part of the ligand field given by[10]

$$\begin{aligned} V(E_g,2) &= 6ee_{\text{eff}}\langle r^2\rangle/R^3, \\ V(E_g,4) &= -\tfrac{5}{3}\sqrt{15}ee_{\text{eff}}\langle r^4\rangle/R^5, \\ V(T_{2g},2) &= 4ee_{\text{eff}}\langle r^2\rangle/R^3, \\ V(T_{2g},4) &= -\tfrac{2}{3}\sqrt{15}ee_{\text{eff}}\langle r^4\rangle/R^5. \end{aligned} \tag{3}$$

R represents the central-ion–ligand distance and e_{eff} the point charges of the six surrounding O^{2-} ions. Although the symmetry of the oxygen cluster is only C_3,[11] the problem has been treated for cubic symmetry. However, as shown by Blume *et al.*,[12] this approximation is well justified.

The wave functions $|j\rangle$ and $|k\rangle$ occurring in (2) were determined by a diagonalization of the electronic Hamiltonian of Fe^{3+} in a trigonally distorted octahedral field including electron-electron interaction, spin-orbit coupling, and an external magnetic field. The angle θ between the threefold axis of the distorted octahedron and the external field was varied. For the calculation, six input parameters are required: the Racah parameters B and C, the octahedral and trigonal splitting parameters $10Dq \equiv \Delta$, v, and v', respectively,[13] and the spin-orbit coupling constant ζ. Concerning B and C, the values of 655 and 3098 cm^{-1} determined from the optical spectrum of Fe^{3+} in corundum (α-Al_2O_3)[14] have been used (the structure of $LiNbO_3$ can be derived from that of corundum).[11] Following the procedure outlined by Cole and Garrett,[15] this B value corresponds to a spin-orbit coupling constant ζ of 310 cm^{-1}. The $10Dq$ value of 14400 cm^{-1} given[14] for Fe^{3+}-Al_2O_3 is certainly too high, as the hexagonal lattice constants a and c are raised by factors of 1.073 and 1.063, respectively, upon replacement of the Al_2O_3 by the $LiNbO_3$ lattice.[16] The actual reduction of the $10Dq$ value cannot be estimated, as the exact position of the Fe^{3+} impurity ion is not known for these two substances. The choice of the $10Dq$ value, however, is important because a level crossing between the first two excited terms ($^2T_{2g}$,$^4T_{1g}$) occurs at $10Dq^c = 13700$ cm^{-1}. The term $^2T_{2g}$ is the lower one for $Dq > Dq^c$. For $Dq < Dq^c$ the term sequence is also determined by the trigonal splitting, which can be calculated from the experimentally observed zero-field splitting of the $^6A_{1g}$ ground state[17] and the sign of the Mössbauer quadrupole splitting[11] of Fe^{3+} in $LiNbO_3$. A reduction of $10Dq$ by about 10% below Dq^c to a value of 12000 cm^{-1} is sufficient for the $^4A_{2g}$ ($^4T_{1g}$) state to lie lower than the $^2A_{1g}$ ($^2T_{2g}$) state (see Fig. 2). With $10Dq = 12000$ cm^{-1} the one-electron splitting parameter v has a value of $+3300$ cm^{-1}. The parameter v', which is usually small compared with v,[13] has been set equal to zero.

Spin-orbit coupling splits the $^4A_{2g}$ multiplet into the (Kramers) degenerate singlets Γ_4^T,Γ_5^T and the doublet Γ_6^T which lies lowest.

The coefficients $V(\Gamma_{ig},l)$ were calculated according to (3) with use of the point-charge expression $Dq = -\frac{1}{6} \times ee_{\text{eff}}\langle r^4\rangle/R^5$ and a bond length R of 21.5 Å (Li octahedra[11]). The ratio of the expectation values $\langle r^2\rangle/\langle r^4\rangle$ was reduced as compared with the free-ion value because of the expanded wave functions of the Fe^{3+} ion coordinated by six oxygens. Following Blume and Orbach,[9] this expansion can be accounted for by a decrease of the formal charge. As the B value of 655 cm^{-1} can be correlated with a charge of almost $+1$,[15] the ratio $\langle r^2\rangle/\langle r^4\rangle$ of $0.21a_0^{-2}$ resulting from Fe^+ self-consistent-field wave functions[9] (a_0: Bohr's radius) has been used.

By use of the wave functions from the diagonalization of the complete Hamiltonian with $10Dq = 12000$ cm^{-1}, the ground-state populations displayed in Fig. 3 are obtained (external field: 4 T). One set of lines belongs to the sum of the intensities $I_{+m_s} + I_{-m_s}$, $|m_s| = \frac{1}{2}, \frac{3}{2}$, and $\frac{5}{2}$, originating from the lower, the other set to the intensity sum originating from the upper state of the magnetically split Γ_6^T doublet. Note the similarity of the two

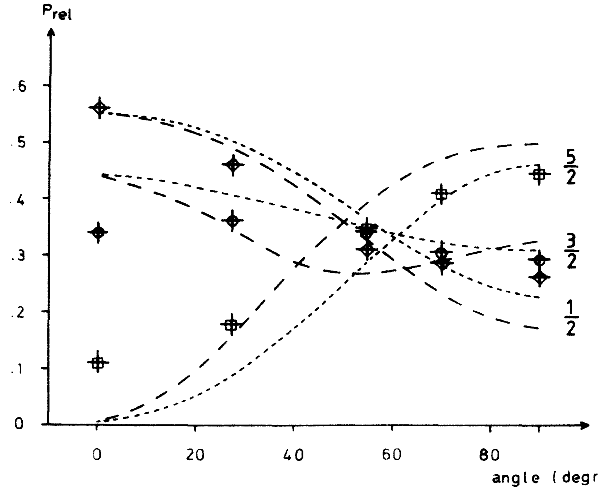

FIG. 3. The sum of the initial populations of the m_s and $-m_s$ sublevels of the $^6A_{1g}$ term as a function of the angle θ between the magnetic field and the crystallographic c axis in $LiNbO_3$:^{57}Co single crystals at 4.2 K in a field of 4 T. Points: experimental data (crossed squares, $I_{+5/2}+I_{-5/2}$; crossed circles, $I_{+3/2}+I_{-3/2}$; crossed lozenges, $I_{+1/2}+I_{-1/2}$). Broken and dotted lines: Calculated sum of the populations originating from the lower and higher states of the magnetically split doublet Γ_6^T, respectively (see text).

plots which is a consequence of the approximate time-reversal symmetry of the states involved. As a consequence, any population ratio $A = P_{\text{upper}}/P_{\text{lower}}$ will give a similar angular dependence for the summed-up intensities. If the angular dependence of the single intensities I_{m_s}, $m_s = -\frac{5}{2}, -\frac{3}{2}, \ldots, +\frac{5}{2}$, is considered, further assumptions regarding A have to be made. In the case of $10Dq = 14000\ \text{cm}^{-1}$ (the remaining parameters being the same) a worse fit to the experimental data was obtained.

The results indicate that the angular dependence of the anomalous ground-state populations can be satisfactorily described by consideration of only electronic matrix elements of the orbit-lattice interaction between the lowest excited Kramers doublet and the $^6A_{1g}$ ground manifold. The point-charge model has been used in a consequent manner omitting any fitting procedure.

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