Comments and Addenda

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Spin-lattice relaxation of ^{59}Co in $K_3Co(CN)_6$

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Previously reported measurements of the NMR spin-lattice relaxation time of ^{59}Co in $K_3Co(CN)_6$ have been extended towards lower temperatures ($T < 100$ K) to determine the contribution of the low-frequency normal modes of vibration of the $Co(CN)_6$ octahedra to the relaxation. It has been found that the temperature dependence of the relaxation in the region $35 \leq T \leq 300$ K can be reasonably well accounted for in terms of the individual contributions of three intermediate-frequency modes (380, 414, and 565 cm^{-1}) and two low-frequency modes (104 and 129 cm^{-1}) and that overlapping of closely spaced modes tends to worsen the agreement with experiment.

In a previous paper[1] (I) measurements of the initial NMR spin-lattice relaxation time of ^{59}Co in a single crystal of $K_3Co(CN)_6$ were reported from 115 to 300 K with one measurement at 78 K. The results suggested that an internal optical model of the $Co(CN)_6$ octahedron having a wave number of 412 cm^{-1} is primarily responsible for relaxation above about 100 K. A detailed quadrupolar calculation based on a point-charge model provided support for this conclusion. The result is interesting because certain low-frequency modes of vibration around 100 cm^{-1} may have been expected to dominate the relaxation rather than an intermediate-frequency mode (or modes) near 412 cm^{-1}.

The initial relaxation rate is given by

$$1/T_1 \simeq W_1 + W_2 + W_2' \ , \qquad (1)$$

where W_1, W_2, and W_2' are the transition probabilities per unit time between the $(\pm\frac{1}{2}, \pm\frac{3}{2})$, $(\pm\frac{1}{2}, \mp\frac{3}{2})$, and $(\pm\frac{1}{2}, \pm\frac{5}{2})$ states. Equation (1) is approximately valid because the relaxation was reasonably well described by a single exponential for pulse spacings up to twice the relaxation time. In this approximation the spin-lattice relaxation time of the ^{59}Co nucleus was found to be[1]

$$\frac{1}{T_1} = \frac{9\pi^3}{16}\left(\frac{eQ}{2I(2I-1)}\right)\sum_l \frac{R^l}{\Delta\omega_l \omega_{l0}^2 \sinh^2(\hbar\omega_{l0}/2kT)} \ , \qquad (2)$$

where

$$R^l = \sum_{ll'} \left|\sum_i \chi_i^{\mu-1}(ll')\right|^2 + 7\sum_{ll'}\left|\sum_i \chi_i^{\mu-2}(ll')\right|^2 .$$

$\Delta\omega_l$, the bandwidth of model l, arises from the assumption of a linear dispersion relation $\omega_l(k) = \omega_{l0} - \Delta\omega_l(k/k_m)$ (I). The coefficient R^l is expressed in terms of (a) certain tensor quantities[2] which describe the strength of the spin-lattice coupling and (b) the eigenvalues of the lth mode of vibration. The calculated values of R^l have been tabulated in I.

In calculating the relaxation time using Eq. (2) three low-frequency normal modes F_{1u}, F_{2g}, and F_{2u} which have wave numbers of 129, 129, and 104 cm^{-1}, respectively, and five intermediate modes F_{1g}, $2F_{1u}$, F_{2g}, and F_{2u} (303, 565, 414, 450, and 380 cm^{-1}) have to be considered.[1,3] In the high-temperature work ($T > 100$ K) (I) the experimentally found dependence of T_1 on an intermediate-frequency mode (414 cm^{-1}) was explained in terms of the relatively large R^l factor found for this mode coupled with the assumption that $\Delta\omega_l^{\rm low} \gtrsim 20\Delta\omega_l^{\rm inter} \cdot \Delta\omega_l^{\rm low}$ may be expected to be larger than $\Delta\omega_l^{\rm inter}$ if the low modes are more strongly coupled to the lattice. Since T_1 is strongly dependent on the frequency of the modes ($T_1 \propto \omega^4$ in the high-temperature limit) it may be expected that below 100 K the relaxation will be dominated by the low-lying modes. We have therefore extended the measurements towards lower temperatures to check the assumption that

$\Delta\omega_l^{low} \gtrsim 20\Delta\omega_l^{inter}$ and to see if supporting evidence could be found for the recent conclusion of Gordon and Hoch[4] that a band of several overlapping modes is involved in relaxation.

The spin-lattice relaxation measurements on a newly grown single crystal of $K_3Co(CN)_6$ were carried out at 19 MHz using a sensitive coherent NMR spectrometer supplied by Spin-Lock Ltd. Measurements were made down to 35 K. In the overlapping temperature regions the present results agree very well with the previous ones (see Fig. 1).

The solid line in Fig. 1 represents the best fit of the experimental points to Eq. (2) in the form

$$\frac{1}{T_1} = k\left(\sum{}' \frac{R^l}{\lambda\omega_l^2 \sinh^2(\hbar\omega/2kT)} + \sum{}'' \frac{R^l}{\omega_l^2 \sinh^2(\hbar\omega/2kT)}\right), \qquad (3)$$

where $\sum'$ refers to the three low-frequency modes, $\sum''$ refers to the five intermediate ones, and $\lambda = \Delta\omega^{low}/\Delta\omega^{inter}$. We have assumed that the five $\Delta\omega^{inter}$ are all very nearly the same and similarly for the $\Delta\omega^{low}$. There are therefore only two adjustable parameters in Eq. (3), k and λ. The contributions of the various modes to T_1 are given in Fig. 1. At 300 K, Q_{12} (380 cm^{-1}) and Q_7 (565 cm^{-1}) together contribute about equally to T_1 compared to Q_8 (414 cm^{-1}) (a point overlooked in I). The two low modes Q_9 (129 cm^{-1}) and Q_{13} (104 cm^{-1}) make a much smaller contribution. The other low mode, Q_{11} (129 cm^{-1}), makes a negligible contribution from 35 to 300 K. Below about 100 K, the low-frequency modes Q_9 and Q_{13} dominate the relaxation. From the best fit $\lambda = \Delta\omega^{low}/\Delta\omega^{inter} = 40 \pm 4$. Although no information regarding the relative bandwidths of the low- and intermediate-frequency modes exists, this factor is considered to be rather high and the following approach has been tried.

In their recent paper, Gordon and Hoch[4] reported measurements of the parameters W_1 and W_2/W_1 for Co in $K_3Co(CN)_6$. The ratio W_2/W_1 is directly related to the χ_l^μ which appear in Eq. (2). The experimentally determined value of this ratio was found to be 0.2 at room temperature, quite different from the calculated value of 24 for the 414 cm^{-1} mode which contributes significantly to the relaxation at 300 K. In attempting to explain the measured ratio of W_2/W_1, these authors assumed complete overlap of pairs of intermediate-frequency modes to obtain limiting calculated values of this ratio. In considering Q_8 (414 cm^{-1}) and Q_{12} (380 cm^{-1}), for example, the predicted ratio becomes 0.69, much closer to the experimental value. It seemed reasonable to conclude that overlapping intermediate-frequency modes play an important role in relaxation above 100 K. Likewise we may expect that overlapping low-frequency modes will also affect the relaxation. We have calculated W_2/W_1 for the overlapping pair Q_9 and Q_{11}, both occuring at 129 cm^{-1}, and found the ratio to be 13 for the three low-frequency modes. Consequently the contribution to the relaxation from the low modes is enhanced relative to the intermediate ones if overlapping modes are considered to occur in both frequency regions. In fact, a fit to the data in this case gave $\lambda = 100 \pm 10$, which is untenable. We conclude that the T_1 measurements from 35 to 300 K can be better explained in terms of the individual contributions of the various modes of vibration to the relaxation. An experiment that would shed additional light on the relaxation process, would be to measure W_2/W_1 as a function of temperature.

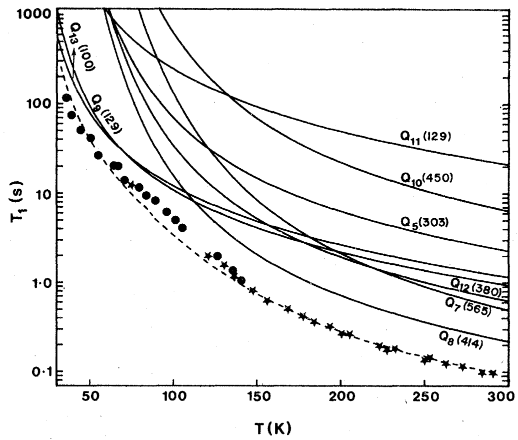

FIG. 1. Spin-lattice relaxation time of ^{59}Co in $K_3Co(CN)_6$ as a function of temperature. Solid circles: present measurements. Stars: previous measurements (I). Dashed line represents the best fit of Eq. (3) to the experimental points. The contributions of the individual modes are indicated by the solid lines. Numbers in parentheses are wave numbers of the various modes in cm^{-1}.

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[1] M. J. R. Hoch, J. A. J. Lourens, and M. I. Gordon, Phys. Rev. B 13, 2787 (1976).

[2] J. van Krandendonk, Physica (Utrecht) 20, 781 (1954).

[3] I. Nakagawa, Bull. Chem. Soc. Jpn. 46, 3690 (1973).,

[4] M. I. Gordon and M. J. R. Hoch, J. Phys. C. 11, 2139 (1978).