Temperature dependence of the electric field gradient in mercuric chloride

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Summary

The temperature dependence of the ^{35}Cl quadrupolar resonance frequency has been measured in a high purity sample of mercuric chloride ($HgCl_2$) over the temperature range 4 K – 460 K. The results allow the temperature dependence of the electric field gradient (efg) at the two inequivalent sites of the chlorine atoms to be determined. Several models were considered to describe the experimental observations, including both librational and vibrational modes. None of the models provides a satisfactory description of the data over the entire temperature range. It appears that a single mode with a wave number of approximately 30 cm^{-1} can account for the data in the high temperature (T > 80 K) region. This compares well with the results of Raman spectroscopy in this temperature range, and it appears that changes in the Raman frequencies with temperature may account for the observed temperature variation of the efg at lower temperatures. Measurements of the second moment of the resonance line and the nuclear quadrupole resonance frequency provide tentative evidence of a small but abrupt change in the efg at approximately 90 K.

TABLE I. Results of a Raman investigation[1] of $HgCl_2$.

Temperature (K)	Translatory modes (cm^{-1})				Rotatory modes (cm^{-1})			ν_1 (cm^{-1})	ν_3 (cm^{-1})
295	18	26	43	74	124		167	315	383
150	18.5	26, 29	48	77	126	134		317	388

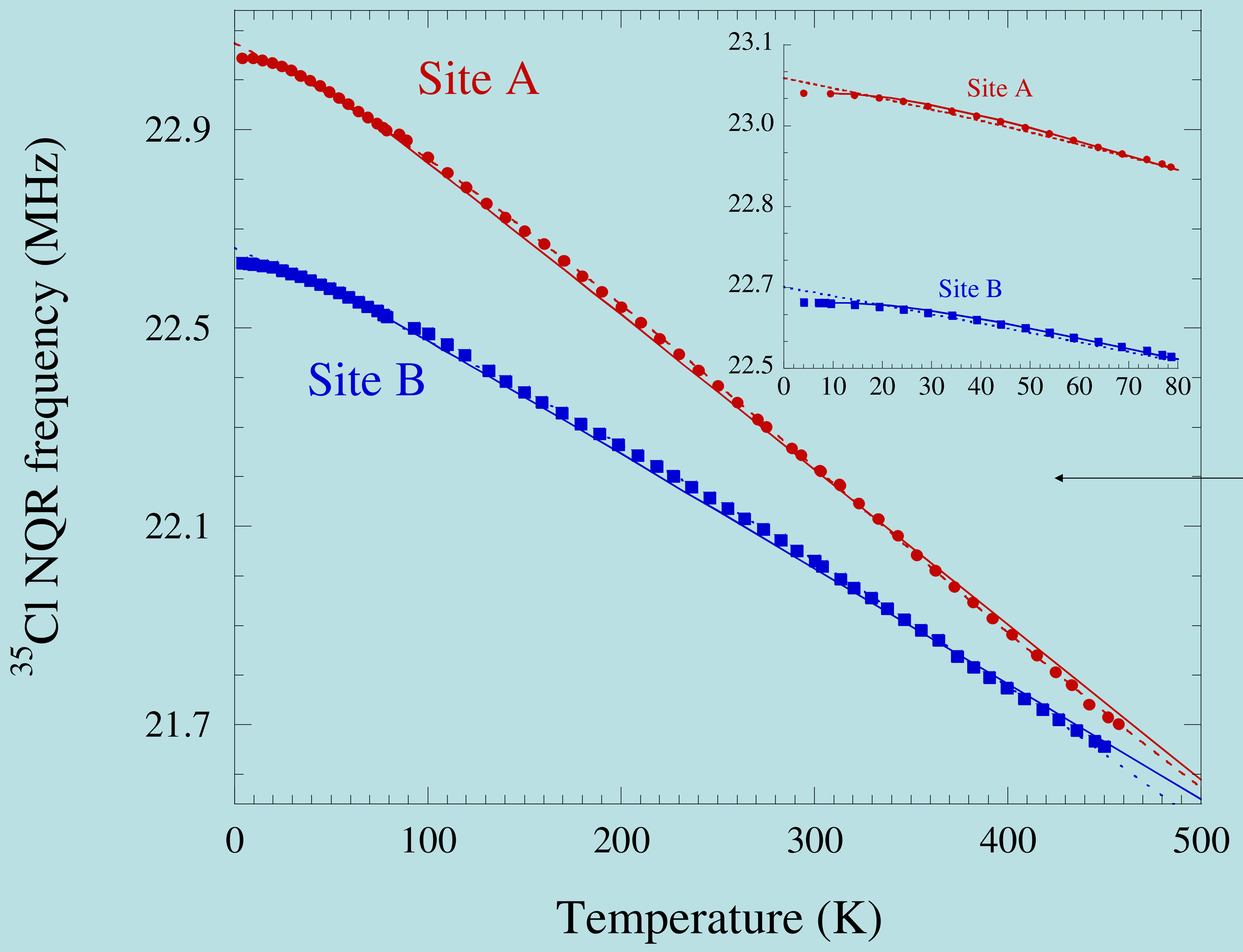

FIG. 1. Nuclear quadrupole resonance frequency results for the ^{35}Cl nucleus at Sites A and B for the entire temperature range studied. The Brown model for librational motion (dashed lines) and the acoustic phonon model (full lines) have been fitted to the data. The parameters of the fits are provided in Table II. An inset highlights the low temperature data.

TABLE II. Fit parameters for the Brown and acoustic phonon models over the entire temperature range.

Site	Brown model		
	a (MHz)	b (kHz K^{-1})	c (Hz.K^{-2})
A	23.057 ± 0.003	– 2.35 ± 0.04	– 1.19 ± 0.08
B	22.651 ± 0.002	– 1.65 ± 0.03	– 1.06 ± 0.06
Site	**Acoustic phonon model**		
	ν_0 (MHz)	S (× 10^{-2})	Θ_D (K)
A	23.011 ± 0.001	9.60 ± 0.05	100 ± 10
B	22.623 ± 0.001	7.20 ± 0.05	100 ± 10

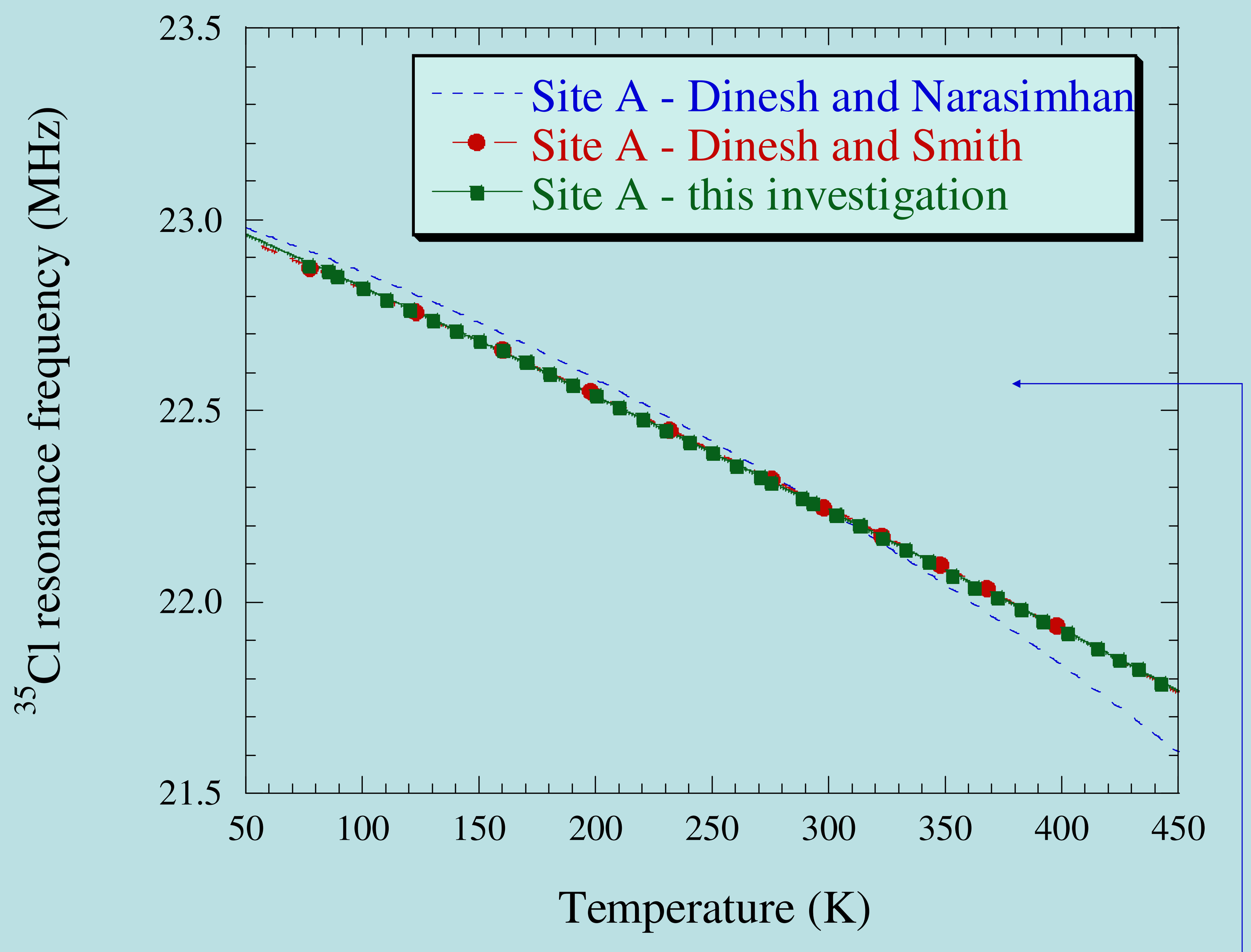

FIG. 2. Comparison of the high temperature results for site A with the results of the two previous investigations[2, 3]. The Brown model has been fitted to all the results.

Theoretical models

Brown model for molecular librations:

$$\nu_Q(T) = a + bT + cT^2$$

Bayer model for a single molecular libration mode:

$$\nu_Q(T) = \nu_0\left[1 - \frac{3\hbar^2}{4Ik_B}\coth\left(\frac{\Theta_T}{2T}\right)\right]$$

Acoustic phonon model:

$$\nu_Q(T) = \nu_0\left[1 - S\left(\frac{T}{\Theta_D}\frac{c_V}{9R} + \frac{1}{\exp(\Theta_D/T) - 1}\right)\right]$$

where $$\frac{c_V}{9R} = \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x-1)^2}\,dx$$

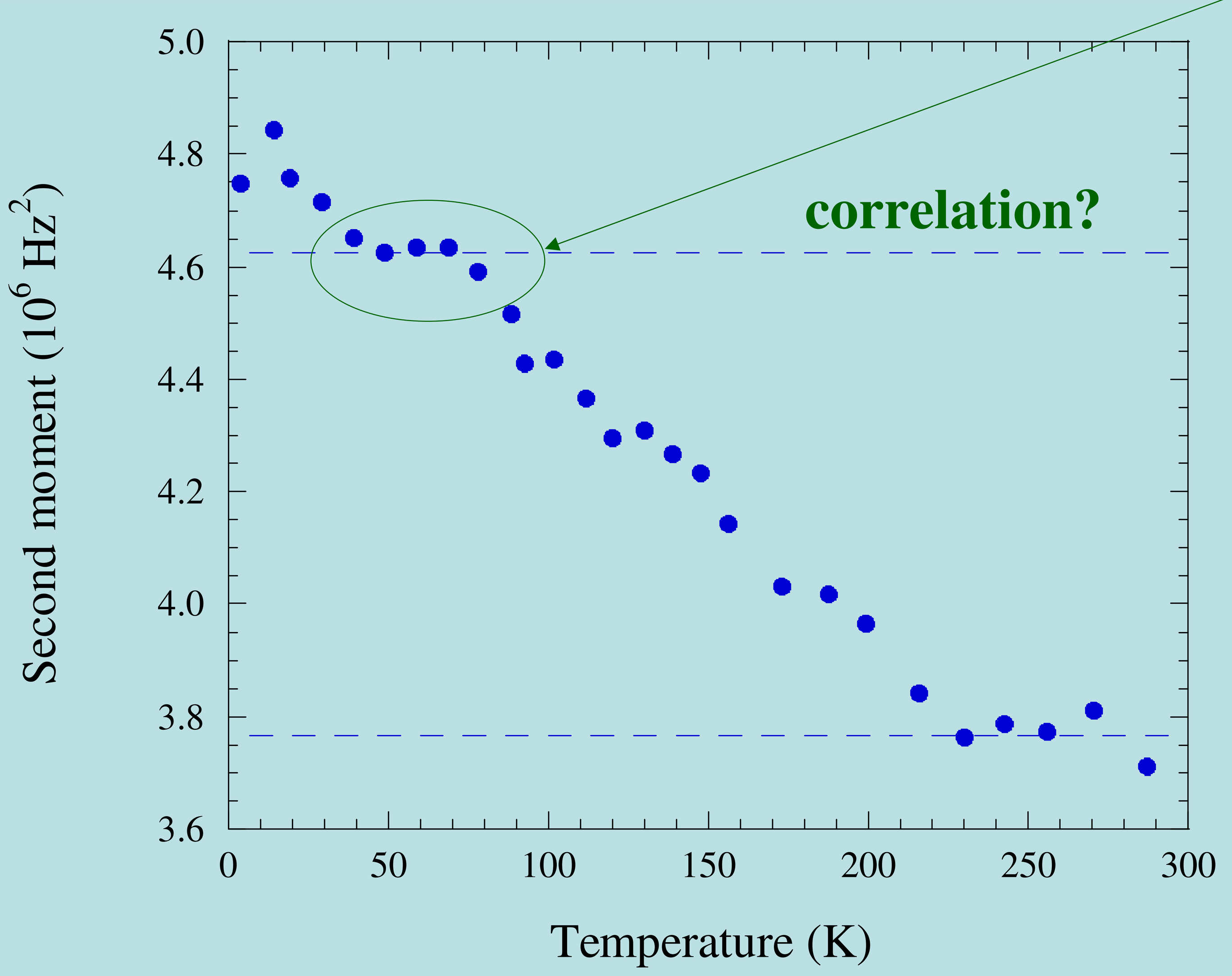

FIG. 5. Second moment of the resonance line for site A as a function of temperature. The plateau between 40 K and 90 K is highlighted.

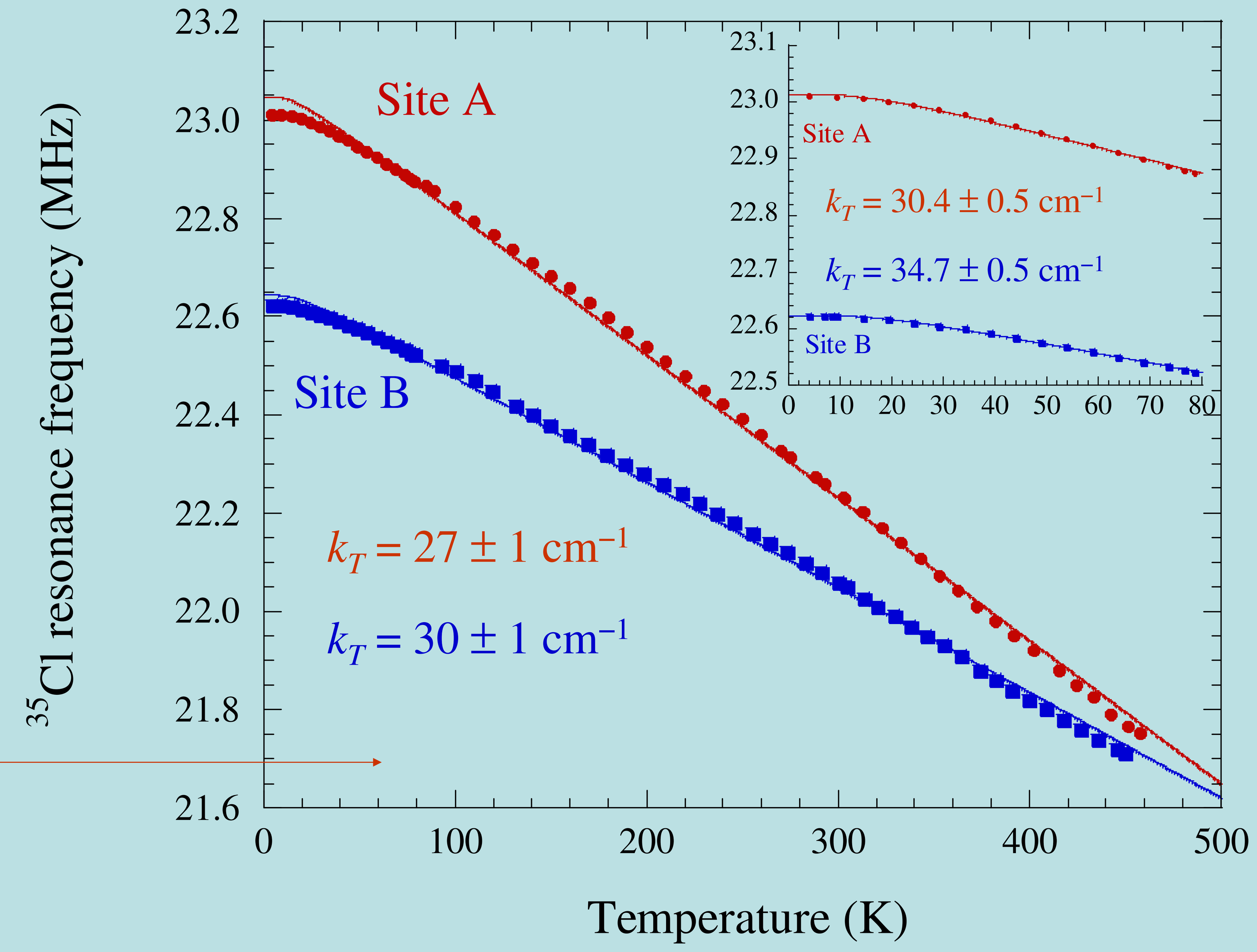

FIG. 3. Fits of the Bayer model for a single librational mode to data for the entire temperature range for both sites. An inset shows the low temperature results and fits. Extracted values for the wave number of the single mode model are given for the fits.

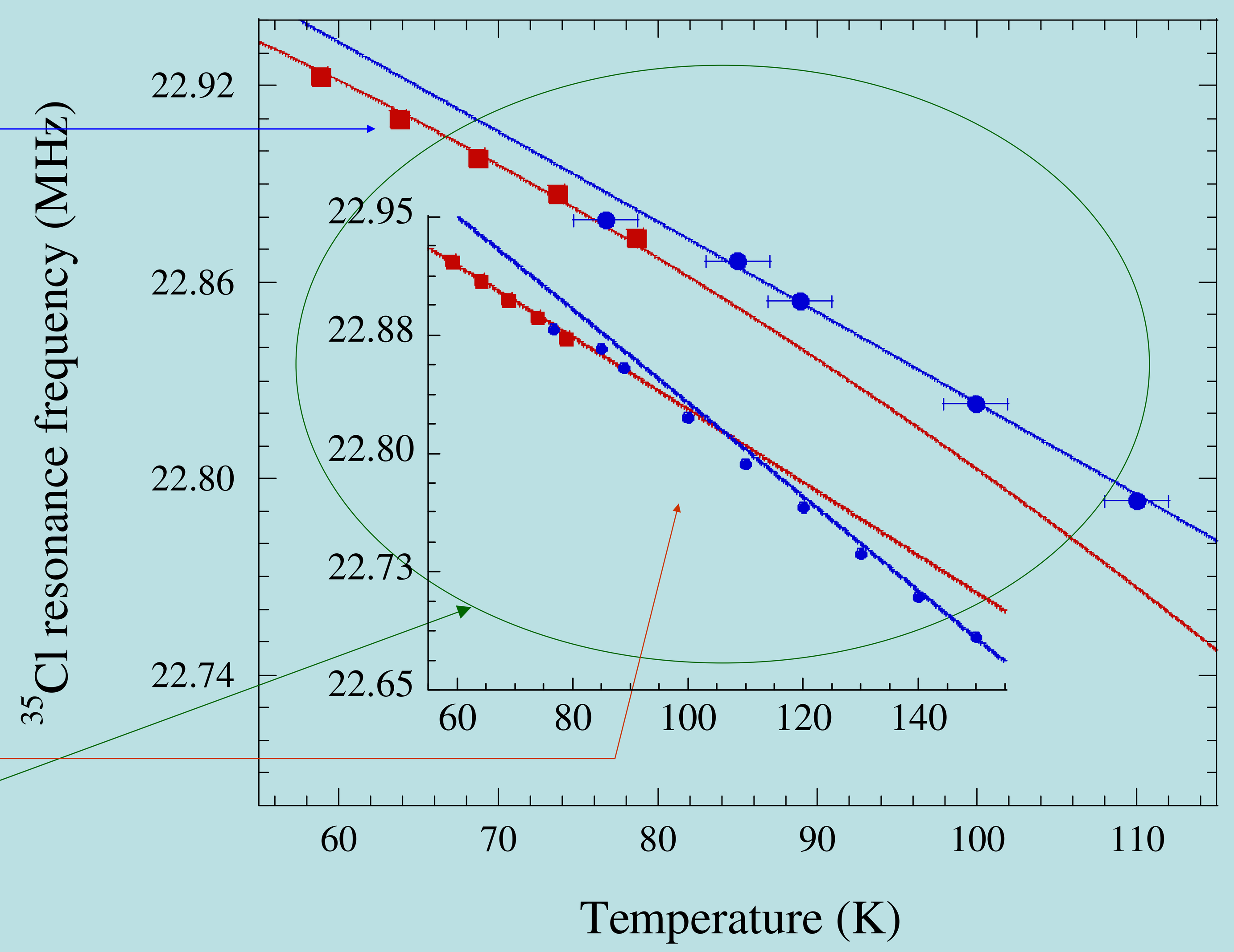

FIG. 4. Crossover from the low temperature to the high temperature region for site A. The fits in the main figure are to the Brown model, and in this scenario the transition appears to be abrupt. Error bars on the high temperature data reflect a difference between the two thermometers used in the investigation. In the inset to the figure the fits are to the Bayer model for the two temperature regions. In this scenario the transition is seen to be relatively smooth. Further investigations of the structure and lattice dynamics would shed some light on the underlying mechanism(s). A correlation is suggested between the second moment results (Fig. 5) and the variation of the efg.

References

[1] D. M. Adams and R. Appleby, J. Chem. Soc., Dalton Trans. **11**, 1530 (1977).

[2] Dinesh and P. T. Narasimhan , J. Chem. Phys. **45**, 2170 (1966).

[3] Dinesh and J. A. S. Smith, Advances in Nuclear Quadrupole Resonance **1**, 31 (1974).