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Temperature dependence of the isotropic exchange constant

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Abstract. The temperature dependence of the isotropic Heisenberg exchange integral between two magnetic atoms is investigated, assuming first a harmonic and secondly an anharmonic dimeric oscillator, which is compared with a crystal by means of the Einstein approximation. The exchange constant J is shown to decrease with increasing temperature mainly as a result of lattice expansion rather than the vibrational variation in internuclear distance. The magnitude of the thermal variation in J is sufficient to warrant the correction of experimental susceptibility and other bulk magnetic data for its effect. Simple and accurate corrections are proposed. As an example, published susceptibility data for the ionic ferromagnet Rb_2CrCl_4 is reanalysed, to reveal a temperature-dependent exchange constant, in accord with the theory.

1. Introduction

The isotropic Heisenberg exchange integral between two magnetic atoms is in general a sensitive function of interatomic distance r . Since r normally varies with time owing to vibrational motion, the observed exchange constant j for a given vibrational state is a time-averaged expectation value of its operator j . In a bulk magnetic measurement on a single crystal, one typically determines a thermally averaged exchange constant $J = \langle j \rangle_T$, and this may be temperature dependent as a result of the thermal population of different vibrational states. Any bulk magnetic quantity which depends upon J will reflect its temperature dependence, and so it is important to be able to account for the latter in the treatment of experimental data.

The temperature dependence of J was previously considered by Zaspel and Drumheller (1977). In accord with several previous workers (Seehra and Castner 1968, Griffiths 1961) they assumed an exchange integral of the form

$$j(x) = J_0 \exp(-\lambda x) \quad (1)$$

where $x = r - r_0$, and r_0 is the equilibrium distance between the two atoms at 0 K. The wavefunctions of the harmonic oscillator with an anharmonic term in x^3 derived from the Morse potential were calculated by second-order perturbation theory, and matrix elements with j were formed. A crystal composed of such binuclear oscillators was then considered in the Einstein approximation. Three parameters were required to describe the temperature dependence of J : the bond strength, the reduced mass of the oscillator, and λ . The latter was calculated for various divalent transition metal to halogen bonds by comparing (1) with the exponential part of a Slater-type overlap integral.

The approach of Zaspel and Drumheller gave a reasonable description of the temperature dependence of J as manifest in the electron paramagnetic resonance linewidth of a number of transition-metal halides. However, it can be criticised on a number of grounds, as demonstrated below. Firstly, it does not reveal the physical origin of the temperature dependence, which in fact is mainly a result of thermal expansion, rather than of vibrational modulation of j . Secondly, the expression of the temperature dependence of J is unnecessarily complicated and, involving three difficult-to-estimate parameters, is of limited value as a correction to experimental data.

I consider two alternative approaches to calculating the temperature dependence of J . The first (section 2) assumes harmonic oscillations about a temperature-dependent equilibrium position. This is often a good representation of reality, corresponding, for example, to the Debye–Waller approximation in crystallography. The displacement x in (1) is written as the sum of a thermal expansion term $\langle x \rangle_T$ and a harmonic fluctuation term x' , and matrix elements are formed with the harmonic oscillator wavefunctions. The thermal distribution of vibrational states in the crystal is included by the Einstein approximation. Although the latter is unphysical in the sense that it does not admit phonon modes, it is appropriate for the present problem since bond length changes will be dominated by optic modes which are typically weakly dispersed (Reissland 1973). By separating the effects of thermal expansion $\langle x \rangle_T$ and fluctuations x' , the physical origin of the temperature dependence of J is clearly revealed. The second approach assumes the anharmonic Morse potential and calculates expectation values of the operator (1) without the use of perturbation theory, resulting in a very simple expression. Thermal averaging is performed in the Einstein approximation as before. The two approaches are compared in section 4. In section 5 the necessity and effectiveness of the theory are demonstrated through a reanalysis of previously published susceptibility data for the ionic ferromagnet Rb_2CrCl_4 .

2. Temperature dependence of J in the harmonic approximation

The following theory calculates the temperature dependence of the isotropic near-neighbour exchange constant J , for harmonic oscillations about a temperature-dependent equilibrium position. The parameter λ was calculated by Zaspel and Drumheller (1977).

The harmonic oscillator wavefunctions are (Landau and Lifshitz 1977)

$$\psi_n(x') = (m\omega/\pi\hbar)^{1/4} (2^{n/2} \sqrt{n!})^{-1} \exp(-m\omega x'^2/2\hbar) H_n(x' - \sqrt{m\omega/\hbar}) \quad (2)$$

where $H_n(\)$ are the Hermite polynomials. With these wavefunctions, one may make matrix elements with the operator

$$j_T = J_0 \exp[-\lambda(x' + \langle x \rangle_T)] \quad (3)$$

where $\langle x \rangle_T$ is the displacement of the equilibrium separation from its zero temperature value, i.e. $\langle x \rangle_0 = 0$. Therefore (dropping the subscript T),

$$\langle n|j|n \rangle = J_0 \sqrt{\frac{m\omega}{\pi\hbar}} (2^n n!)^{-1} \int_{-\infty}^{\infty} \exp[-\lambda(x' + \langle x \rangle)] \exp\left(-\frac{m\omega x'^2}{\hbar}\right) H_n^2\left(x' \sqrt{\frac{m\omega}{\hbar}}\right) dx' \quad (4)$$

$$= J_0 (\sqrt{\pi} 2^n n!)^{-1} \exp(-\lambda \langle x \rangle) \int_{-\infty}^{\infty} \exp \left[- \left(y^2 + \frac{\lambda y}{\sqrt{m\omega/\hbar}} \right) \right] H_n^2(y) dy \tag{5}$$

where $y = x' \sqrt{m\omega/\hbar}$. Completing the square in (5) gives

$$\begin{aligned} \langle n|j|n \rangle &= J_0 (\sqrt{\pi} 2^n n!)^{-1} \exp(-\lambda \langle x \rangle) \exp \left(\frac{\lambda^2 \hbar}{4m\omega} \right) \int_{-\infty}^{\infty} \\ &\times \exp \left[- \left(y + \sqrt{\frac{\lambda^2 \hbar}{4m\omega}} \right)^2 \right] H_n^2(y) dy. \end{aligned} \tag{6}$$

The following definite integral has been established (Apelblat 1983):

$$\int_{-\infty}^{\infty} \exp[-(u - ia)^2] H_p(u) H_n(u) du = \sqrt{\pi} 2^p p! (ia)^{p-n} L_n^{p-n}(2a^2) \quad p \geq n \tag{7}$$

where $L_n^\alpha(\cdot)$ is an associated Laguerre polynomial:

$$L_n^\alpha(v) = \sum_{p=0}^n (-1)^p \binom{n+\alpha}{n-p} \frac{v^p}{p!} \tag{8}$$

which for $\alpha = 0$ reduces to the Laguerre polynomial

$$L_n^0(v) = \sum_{p=0}^n (-1)^p \binom{n}{p} \frac{v^p}{p!}. \tag{9}$$

Comparing (6) with (7) for $-ia = \sqrt{\lambda^2 \hbar / 4m\omega}$ and $p = n$ gives

$$\langle n|j|n \rangle = J_0 \exp(-\lambda \langle x \rangle + Y/2) L_n^0(-Y) \tag{10}$$

where $Y = \lambda^2 \hbar / 2m\omega$ (typically about 10^{-2} ; see appendix). Using these diagonal matrix elements, the binuclear harmonic oscillator may be compared with the crystal using the Einstein approximation:

$$J(T) = \sum_{n=0}^{\infty} P_n \langle n|j|n \rangle \tag{11}$$

where P_n is the normalised Boltzmann probability that a state $|n\rangle$ occurs. It follows that

$$J(T) = J_0 \exp \left(-\lambda \langle x \rangle + \frac{Y}{2} \right) \sum_{n=0}^{\infty} P_n L_n^0(-Y). \tag{12}$$

Several reasonable approximations to the above equation follow from the fact that

$Y \ll 1$. Firstly, as shown in the appendix, this implies that $Yn \ll 1$ for all significant n . $L_n^0(-Y)$ is then given by

$$L_n^0(-Y) = 1 + nY + n(n-1)Y^2/4 + n(n-1)(n-2)Y^3/36 + \dots \approx 1 + nY. \quad (13)$$

Equation (12) becomes

$$\begin{aligned} J(T) &= J_0 \exp\left(-\lambda\langle x \rangle + \frac{Y}{2}\right) \sum_{n=0}^{\infty} P_n(1 + nY) \\ &= J_0 \exp\left(-\lambda\langle x \rangle + \frac{Y}{2}\right) (1 + \langle n \rangle Y) \end{aligned} \quad (14)$$

where $\langle n \rangle$ is the Planck occupation number (Kittel 1976):

$$\langle n \rangle = [\exp(\hbar\omega/k_B T) - 1]^{-1}. \quad (15)$$

Secondly, since $Y \ll 1$, the approximation $\exp(Y/2) \approx 1 + Y/2$ is valid and (14) becomes

$$J(T) = J_0 \exp(-\lambda\langle x \rangle) [(\langle n \rangle + \frac{1}{2})Y + 1] \quad (16)$$

but as $Y\langle n \rangle \ll 1$ (appendix) the first term in square brackets is also much less than unity, and so

$$J(T) \approx J_0 \exp(-\lambda\langle x \rangle). \quad (17)$$

The above equation shows that the exchange constant depends only upon the thermal expansion to a good approximation. Recalling equation (16), it can be seen that the variation in J with temperature depends upon two factors: a dominant thermal expansion term, and a smaller term in Y resulting from oscillations. Whilst the former causes a decrease in $J(T)$ with increasing temperature, the latter tends to oppose this effect. This would be expected from a consideration of the effect of harmonic oscillations on the form (1). Such a distinction between expansion and oscillation factors was anticipated by Hutchings *et al* (1968).

Experiments at fixed temperatures have suggested that J usually depends upon the bond length $\langle r \rangle$ in the manner $J \propto \langle r \rangle^{-q}$ ($q = 10$ (Bloch 1966); $q = 12$ (De Jongh and Block 1975)). Equation (17) may be related to the power-law dependence of J on $\langle r \rangle$ by differentiating

$$dJ/d\langle x \rangle = -\lambda J \quad (18)$$

from which follows (since $\delta\langle x \rangle \equiv \delta\langle r \rangle$)

$$\delta J/J \approx -\lambda\langle r \rangle \delta\langle r \rangle / \langle r \rangle. \quad (19)$$

Comparing (19) with the derivative of $J \propto \langle r \rangle^{-q}$ enables us to see that $\lambda\langle r \rangle \approx q$. Considering transition-metal fluorides as an example, typical values of λ and $\langle r \rangle$ are about $4 \times 10^{10} \text{ m}^{-1}$ and about $4 \times 10^{-10} \text{ m}$, respectively, which gives $q \approx 16$. This is in reasonable agreement with the typical value of q of about 12 observed experimentally (De Jongh and Bloch 1975).

In the application of (17), the thermal expansion $\langle x \rangle$ is best determined experimentally. At high temperature, $\langle x \rangle$ often varies linearly with temperature (Kittel 1976), and the crystallographic determination of bond lengths at only two temperatures may be sufficient to determine the proportionality constant. The only unknown parameter is then λ , which may be obtained from the tables of Zaspel and Drumheller (1977), or simply estimated as approximately $q/\langle r \rangle$ (see above), with $q \approx 12$.

3. Temperature dependence of J in an anharmonic approximation

The following theory makes no distinction between the thermal expansion and the oscillation contributions to the temperature dependence of J . The anharmonic Morse potential is assumed:

$$V(x) = A[\exp(-2\alpha x) - 2 \exp(-\alpha x)]. \tag{20}$$

The unnormalised wavefunctions for a particle in the Morse potential (Landau and Lifshitz 1977) are

$$\psi = \exp(-\xi/2) \xi^s F(-n, (2s + 1), \xi) \tag{21}$$

where

$$\begin{aligned} s &= \sqrt{-2mE_n/\alpha\hbar} \\ E_n &= A[1 - (\alpha\hbar/\sqrt{2mA})(n + \frac{1}{2})]^2 \\ \xi &= [2\sqrt{2mA}/\alpha\hbar] \exp(-\alpha x) \end{aligned} \tag{22}$$

and F is a confluent hypergeometric function. The integration of such functions is discussed in appendix f of Landau and Lifshitz (1977). It is convenient, for reasons which will become obvious, to consider the integrals $\int_{-\infty}^{\infty} \psi^2 dx$ and $\int_{-\infty}^{\infty} \xi \psi^2 dx$. Changing the variable from x to ξ ($dx = -d\xi/\alpha\xi$) and the limits correspondingly from 0 to ∞ , these become

$$I_1 = \int_{-\infty}^{\infty} \psi^2 dx = -\alpha^{-1} \int_0^{\infty} \exp(-\xi) \xi^{2s-1} F^2(-n, (2s + 1), \xi) d\xi \tag{23}$$

$$I_2 = \int_{-\infty}^{\infty} \xi \psi^2 dx = -\alpha^{-1} \int_0^{\infty} \exp(-\xi) \xi^{2s} F^2(-n, (2s + 1), \xi) d\xi. \tag{24}$$

Now the ratio I_2/I_1 is the matrix element $\langle n|\xi|n\rangle$. Considering the standard integral

$$J_\nu = \int_0^{\infty} \exp(-kz) z^{\nu-1} F^2(-n, \gamma, kz) dz \tag{25}$$

with $k = 1$, $z = \xi$ and $\gamma = 2s + 1$, the desired ratio is

$$I_2/I_1 = \langle n|\xi|n\rangle = J_\gamma/J_{\gamma-1}. \tag{26}$$

From the standard recursion relations of the integrals J_ν , given by Landau and Lifshitz, the following relation is established:

$$J_\gamma = (\gamma - 1)J_{\gamma-1} \tag{27}$$

from which

$$\langle n|\xi|n\rangle = 2s = 2\sqrt{2mE_n/\alpha\hbar} = 2[(\sqrt{2mA}/\alpha\hbar) - (n + \frac{1}{2})]. \tag{28}$$

Since $\xi = [2\sqrt{2mA}/\alpha\hbar] \exp(-\alpha x)$, the expectation value of $\exp(-\alpha x)$ is

$$\langle n|\exp(-\alpha x)|n\rangle = 1 - [\alpha\hbar/\sqrt{2mA}](n + \frac{1}{2}). \tag{29}$$

This equation effectively gives the matrix elements of j (equation (1)), since Zaspel and

Drumheller suggested that $\lambda \approx \alpha$. In order to calculate the thermal average of $\langle n|j|n \rangle$, the energy levels of the Morse potential oscillator (equation (22)) are expanded to $O(n)$:

$$E_n = -A[(1 - \alpha\hbar/\sqrt{2mA})^2 - 2n\alpha\hbar(1 - \alpha\hbar/\sqrt{2mA})/\sqrt{2mA}] \quad (30)$$

and compared with those of the harmonic oscillator ($E_n = (n + \frac{1}{2})\hbar\omega$) to give

$$\hbar\omega \approx 2A\alpha\hbar/\sqrt{2mA}. \quad (31)$$

Here it has been assumed that $\alpha\hbar/\sqrt{2mA} \ll 1$, which may be verified given the typical values $\alpha \approx 4 \times 10^{10} \text{ m}^{-1}$, $m \approx 3 \times 10^{-25} \text{ kg}$ and $A \approx 1.4 \times 10^{-20} \text{ J}$ (see section 5), whence $\alpha\hbar/\sqrt{2mA} \approx 0.05$. The thermal average of the matrix elements (29) are simply (replacing α by λ)

$$\langle \exp(-\lambda x) \rangle = 1 - (\lambda\hbar/\sqrt{2mA})(\langle n \rangle + \frac{1}{2}) \quad (32)$$

where $\langle n \rangle$ is the Planck occupation number (equation (15)). The temperature dependence of J is therefore given by

$$J(T) = J_0\{1 - (\lambda\hbar/\sqrt{2mA})[\exp(2A\lambda\hbar/\sqrt{2mA}k_B T) - 1]^{-1}\}. \quad (33)$$

This equation involves three parameters: the depth A of the vibrational potential well, the reduced mass (m) of the oscillator and λ . It is valid for weak anharmonicity provided that $\lambda \approx \alpha$, an approximation which seems to give reasonable results (Zaspel and Drumheller 1977).

4. Comparison of the two approaches

The theory of the previous section approximately calculated $\langle \exp(-\lambda x) \rangle$ in a weakly anharmonic potential. However, as shown in section 2, it is valid to neglect fluctuations, and so $\langle \exp(-\lambda x) \rangle \approx \exp(-\lambda \langle x \rangle)$. Since $\lambda \langle x \rangle$ will be quite small, $\exp(-\lambda \langle x \rangle)$ can be expanded to first order in $\lambda \langle x \rangle$ and compared with equation (32) to give the thermal expansion

$$\langle x \rangle = (\hbar/\sqrt{2mA})(\langle n \rangle + \frac{1}{2}) \quad (34)$$

with

$$\langle n \rangle = [\exp(2A\lambda\hbar/\sqrt{2mA}k_B T) - 1]^{-1}. \quad (35)$$

It is observed that the high-temperature asymptote of (34) is

$$\langle x \rangle = k_B T/2A\lambda \quad (36)$$

which is reasonably consistent with the classical value $3k_B T/4A\alpha$, calculated from the second and third derivatives of the Morse potential, according to the simple method given by Kittel (1976). Furthermore, equation (34) is observed to be of the correct form, since the linear thermal expansion coefficient $d\langle x \rangle/dT$ would be proportional to $d\langle n \rangle/dT$ which in turn is proportional to $d(N\hbar\omega\langle n \rangle)/dT$, the specific heat C_V . This is essentially Grüneisen's relation (Rosenberg 1962).

It is finally noted that the present theory is only strictly applicable to the case of relatively weak coupling (e.g. $J \ll A$), since the exchange energy is not included in the intermolecular potential.

Table 1. Calculated coefficients in the high-temperature series expansion for the $S = 2$ quadratic layer Heisenberg model ferromagnet (Ishikawa and Oguchi 1971). The series is defined by equation (38).

Coefficient	a_0	a_1	a_2	a_3	a_4	a_5	a_6
Value	1	16	184	1937.07	18284.3	161563.7	1371769

5. Application to high-temperature susceptibility of Rb_2CrCl_4

The ionic ferromagnet Rb_2CrCl_4 ($T_C \approx 52$ K) adopts a K_2NiF_4 -type crystal structure in which Cr^{2+} atoms lie on a square lattice in well separated layers. The Cr–Cr exchange is at least 99% confined to near neighbours and of the isotropic Heisenberg mechanism (Hutchings *et al* 1981, Fyne 1984), with $J/k_B \approx 7.5$ K. The dominantly planar single-ion anisotropy ($D/k_B \approx 1$ K) is not expected to affect the paramagnetic susceptibility above about 80 K.

The exchange constant J was accurately determined as $7.56(19)k_B$ at about 4.2 K from spin-wave measurements (Hutchings *et al* 1981). However, a fit of the paramagnetic susceptibility between about 100 K and room temperature to the high-temperature series expansion for the two-dimensional Heisenberg square-lattice ferromagnet (Crama 1980) gave the lower value of about 6.45 K. This suggests that the exchange constant J should be regarded as temperature dependent.

Following equation (18), J may be written as $J_0 \exp(-\lambda(x))$. For a Cr^{2+} –Cl bond, $\lambda = 3.38 \times 10^{10} \text{ m}^{-1}$ (Zaspel and Drumheller 1977). In the classical high-temperature region, $\langle x \rangle = KT$ where K is a constant (Kittel 1976). For Rb_2CrCl_4 it is possible to calculate approximately the thermal expansion from the lattice constants measured by Janke *et al* (1983) at 77 and 293 K, which gives $K = 2.9 \times 10^{-14} \text{ mK}^{-1}$. Therefore the predicted temperature dependence of J for Rb_2CrCl_4 is given by

$$J = J_0 \exp(-\lambda KT) = J_0 \exp(-PT) \tag{37}$$

with $P = 9.8 \times 10^{-4} \text{ K}^{-1}$, the temperature coefficient of J .

Cornelius *et al* (1986) have tabulated the experimental zero-field susceptibility of Rb_2CrCl_4 between about 50 and about 160 K. Down to at least 80 K, the susceptibility would be expected to be described by the high-temperature series expansion for the 2D Heisenberg square lattice ferromagnet:

$$\chi = (Kg^2/T)[f(J/k_B T) + \varphi(J/k_B T)]$$

where $K = \mu_0 L \mu_B^2 S(S + 1)/3k_B M_R = 9.4266 \times 10^{-6}/M_R \text{ m}^3 \text{ kg}^{-1}$ for $S = 2$:

$$f\left(\frac{J}{k_B T}\right) = \sum_{n=0}^6 a_n \left(\frac{J}{k_B T}\right)^n$$

$$\varphi\left(\frac{J}{k_B T}\right) = \sum_{n=7}^{\infty} a_n \left(\frac{J}{k_B T}\right)^n \tag{38}$$

and M_R is the relative molecular mass in kilograms. The coefficients a_n up to $n = 6$ were calculated using the expressions given by Ishikawa and Oguchi (1971) and are listed in table 1. The small unknown term φ was estimated by the extrapolation $a_n/a_{n-1} \propto 1/n$. Full details of the fitting procedure will be given in a forthcoming publication.

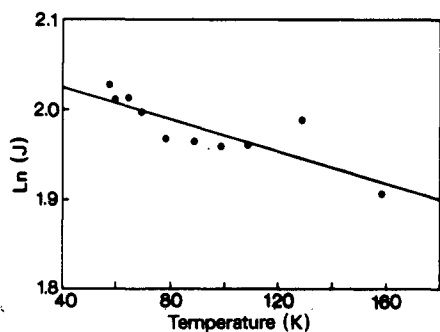


Figure 1. Temperature dependence of the logarithm of the exchange constant J of Rb_2CrCl_4 . At each temperature, J was calculated from the data of Cornelius *et al* (1986) by fitting to the series expansion for the $S = 2$ quadratic layer ferromagnet with $g = 2$. The straight line is the regression line of $\ln(J)$ on T with gradient $-9.0 \times 10^{-4} \text{ K}^{-1}$, intercept 2.06 and coefficient of determination $R^2 = 0.7$. The gradient of the line is the temperature coefficient P defined in equation (37).

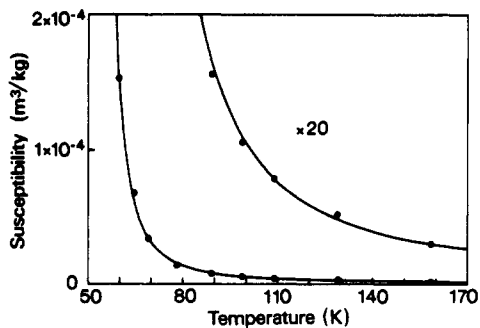


Figure 2. Fit of the susceptibility of Rb_2CrCl_4 (Cornelius *et al* 1986) to the extrapolated high-temperature series expansion for the $S = 2$ quadratic layer Heisenberg ferromagnet (—), with temperature-dependent exchange constant (equation (37)). The best fit between 59 and 160 K is illustrated, corresponding to $J'_0/k_B = 7.927 \text{ K}$, $g = 2.000$ and $P = -9.0 \times 10^{-4} \text{ K}^{-1}$.

An initial fit of (38) to the data in the temperature range 80–170 K, allowing J and g to vary, gave quite a good fit with $J = 7.12 \text{ K}$ and $g = 2.00$. With g fixed at 2.00, each data point was then fitted separately to give J as a function of temperature. The results indicated that J decreased with increasing temperature, as expected. Following equation (37), $\ln(J)$ was plotted against T to give P , the temperature coefficient of J as the gradient (figure 1). Although the points were scattered, the regression line of $\ln(J)$ on T had a gradient of $-9.0 \times 10^{-4} \text{ K}^{-1}$, and a correlation coefficient R of 0.84. The latter shows (Chatfield 1983) that $\ln(J)$ and T are significantly correlated at the 95% confidence level, and that about 70% (R^2) of the variation in $\ln(J)$ with T is accounted for by the linear formula. P estimated in this way ($-9.0 \times 10^{-4} \text{ K}^{-1}$) was very close to that predicted ($-9.8 \times 10^{-4} \text{ K}^{-1}$) by considering the thermal expansion (see above). Such a close agreement was probably fortuitous but confirms the applicability of the analysis. Finally the data were refitted with $g = 2.00$, and a temperature-dependent J (equation (37)) with $P = -9.8 \times 10^{-4} \text{ K}^{-1}$. A very good fit (figure 2) was obtained down to 59 K, with $J'_0/k_B = 7.927 \text{ K}$. J'_0 here is just a parameter and does not represent the zero-temperature value of J , since equation (37) is not valid at very low temperatures. J/k_B in fact increases from 6.79 K at 159 K to 7.48 K at 60 K, a change of about 10% over 100 K.

The prediction (36) for the high-temperature thermal expansion was also tested. An order-of-magnitude estimate of the bond strength A/k_B was taken to be the melting temperature of Rb_2CrCl_4 (824 K (Siefert and Klatyk 1964)). Note that whilst in a binuclear complex A is equal to the bond dissociation energy, in an ionic crystal it is the energy required to break a bond without infinite separation of the ions, and so is in general a smaller quantity. $\langle x \rangle$ was calculated to be $k_B/2\lambda A \approx 1.8 \times 10^{-14} \text{ m K}^{-1}$, in reasonable agreement to that observed ($2.9 \times 10^{-14} \text{ m K}^{-1}$). It is interesting to note that the classical expression $3k_B/4\lambda A$ (see above) would have given a better estimate ($2.8 \times 10^{-14} \text{ m K}^{-1}$).

Finally, assuming CrCl_4 oscillators ($m \approx 3.2 \times 10^{-25}$ kg), equation (33) was used to extrapolate $J(T)$ to 0 K, giving $J_0 \approx 7.6$ K, in very good agreement with the estimate of Hutchings *et al* (1981) of 7.6(2) K.

6. Conclusions

In general the isotropic exchange constant J is temperature dependent as a result of the thermal expansion of the lattice, with thermal fluctuations in the internuclear distance contributing negligibly. In real compounds, J may vary by typically 30% between liquid-helium temperature and room temperature, and so it is essential to correct experimental data for this effect. This is particularly true of susceptibility versus temperature data, which is commonly used to derive exchange constants. Three possible corrections may be considered. If thermal expansion data are available, (17) should be used, especially in systems for which the thermal expansion is not a simple function of temperature. If such data are not available, at high temperatures the thermal expansion may be assumed to vary linearly with temperature, and (36) may be used in conjunction with (17); at lower temperatures the full expression (33) should be used. These corrections involve one parameter (λ), two parameters (λ and A) and three parameters (λ , A and m), respectively, and so wherever possible the first is to be preferred. The corrections are most directly applicable to compounds in which the dominant exchange interaction is between nearest neighbours and isotropic.

Evidence for the variation in J with temperature was found in the high-temperature susceptibility of the ionic ferromagnet Rb_2CrCl_4 . A temperature variation in J was similarly observed in the susceptibility of RbMnF_3 (De Jongh and Breed 1974) and tentatively ascribed to lattice expansion. In general, however, in order to derive the temperature dependence of J from susceptibility measurements, one must know the spin Hamiltonian, so as to be sure that a particular series expansion applies.

Appendix. Justification of the approximation used to derive equation (14)

To derive equation (13), terms of order two or greater in the expansion of the Laguerre polynomial $L_n^0(-Y)$ are dropped. This is justifiable if successive terms T_k diminish rapidly with increasing k . In general the ratio of successive terms is, from (9),

$$T_{k+1}/T_k = Y(n-k)/(k+1)^2 \quad (1 \leq k \leq n). \quad (\text{A1})$$

The right-hand side of (A1) is maximum for $k = 1$, and so the required condition is

$$Y(n-1)/4 \ll 1$$

or

$$Yn \ll 1 \quad (\text{A2})$$

for all significant n , as stated in the text. 'Significant n ' here refers to states with an

appreciable Boltzmann factor $\exp(-n\hbar\omega/k_B T)$ (see equation (12)), and so it is necessary to prove that

$$Yn \exp(-n\hbar\omega/k_B T) \ll 1. \quad (\text{A3})$$

It is easily shown by differentiating with respect to n that the maximum value of this function is

$$Yk_B T/\hbar\omega \quad (e = 2.718 \dots) \quad (\text{A4})$$

in which case, since $\hbar\omega \approx k_B T$ to an order-of-magnitude approximation, the original assertion (A2) is true simply if $Y \ll 1$, with $Y = \lambda^2 \hbar / 2m\omega$ (see text). Assuming typical values ($\lambda \approx 4 \times 10^{10}$ m, $k_B = 1.38 \times 10^{-23}$ J K⁻¹, $\hbar = 1.05 \times 10^{-34}$ J s, $m \approx 3 \times 10^{-25}$ kg and $\omega \approx 10^{13}$ s⁻¹), an approximate value of Y is about 0.03, which is indeed much less than unity. The assumption $Y \ll 1$ also underlies equations (16) and (17).

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