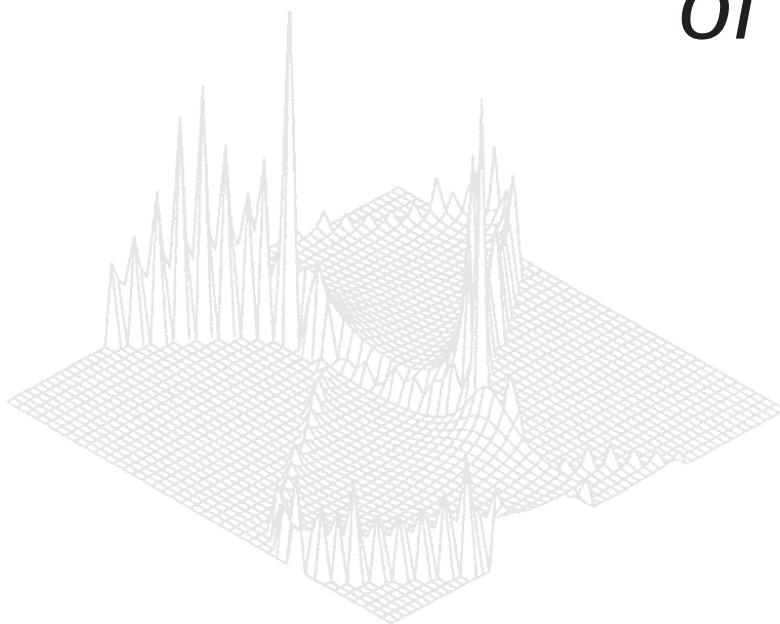

CSIRO PUBLISHING

Australian Journal of Physics

Volume 51, 1998
© CSIRO 1998



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Evaluation of Exchange and Anisotropy Constants of Molecular Species from High Field Mössbauer Spectra*

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Abstract

The molecular field equations for the allowed spin directions for dimer and trimer molecular species have been solved numerically for a range of values of the exchange and anisotropy interactions and of the applied magnetic field. The results may be used for the evaluation of the exchange and anisotropy constants from high field Mössbauer spectra or for selecting the best conditions for proposed experiments in order to determine these parameters.

1. Introduction

Many molecular species contain coupled iron ions in the form of dimers, trimers or more complicated arrangements. In trying to deduce the bridging ligands for such species, determination of the exchange and anisotropy constants can be an important piece of information. Although application of a magnetic field can break the magnetic coupling, the measurement of bulk properties, such as the magnetisation, does not provide an easy method of evaluating these microscopic magnetic parameters, particularly on powder samples. However, Mössbauer spectra in applied magnetic fields provide two independent pieces of information on the internal magnetic arrangements, namely the measured hyperfine field and the intensities of the $\Delta m = 0$ lines. Together, these should be sufficient to determine the exchange and anisotropy constants, at least when the results from several spectra at different fields are used. A recent study which illustrates this point was for the iron(III) sites in ferreascidin (Taylor *et al.* 1995) in which three iron species, two dimeric and one trimeric, were found but could not be completely identified at that stage.

The magnetic properties of simple two sublattice antiferromagnets in an applied magnetic field are well known. In the case of strong anisotropy, one obtains a spin flip at some critical value of the applied field when it is strong enough to break the exchange coupling. In the case of weak anisotropy, one obtains a spin flop when the applied field overrides the anisotropy, provided the applied field direction is sufficiently close to the anisotropy direction, followed by a linear approach to saturation as the directions of the two sublattices come closer together.

* Refereed paper based on a contribution to the International Workshop on Nuclear Methods in Magnetism, held in Canberra on 21–23 July 1997.

There have been three related previous analyses of this type. Beckmann *et al.* (1968) obtained the anisotropy constant of FePO_4 from analysis of the spectra during field-induced spin rotation, while Mørup (1985) analysed the spin-flop transition in antiferromagnetic microcrystals. A detailed approach to the fitting of applied field Mössbauer spectra using a molecular field theory approach has been given by Pankhurst and Pollard (1990). This allows evaluation of the exchange and anisotropy constants, preferably by fitting several spectra simultaneously, and has proved very useful, for example, in identifying poorly crystalline iron oxide species in a variety of contexts (Pollard *et al.* 1992; Pankhurst and Pollard 1993; Pankhurst 1994). We would like to point out that their method should be equally useful for molecular dimer and trimer species. However, since their program is unfortunately not widely used, we set out here a complete set of the numerical solutions for the spin arrangements in a form that can be used by Mössbauer spectroscopists who only have access to a conventional least squares program for fitting sums of sextets.

This paper evaluates all the possible configurations for ferric ions in dimer and trimer systems as a function of applied field, nearest neighbour exchange constant and anisotropy constant. The results can be used in two different ways. The first is to extract the values of exchange and anisotropy constants from conventional fitting of Mössbauer spectra taken at different fields. The second is to enable the prediction of the most useful regions of applied field in which to take spectra when there is some reasonable knowledge beforehand of the approximate values of the exchange and anisotropy constants.

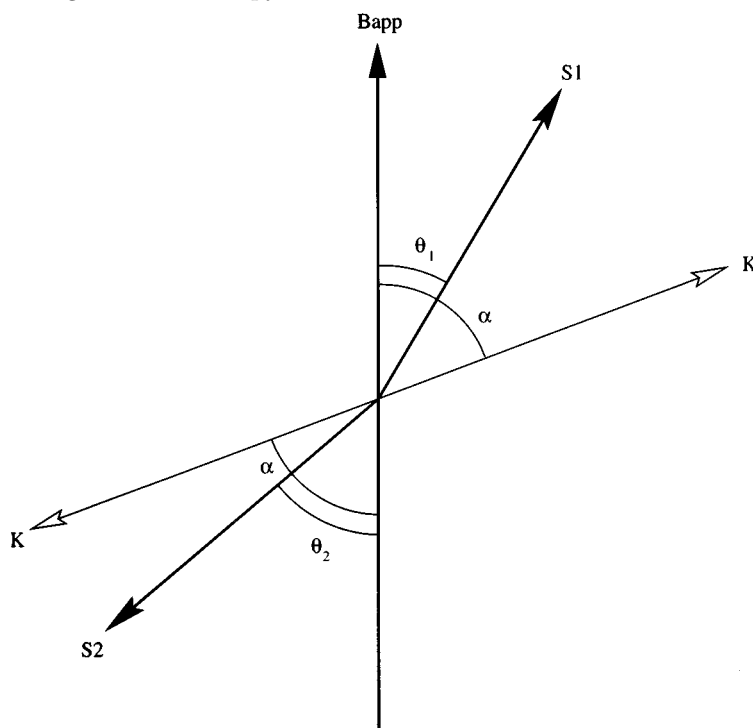


Fig. 1. Spin arrangement for dimer configuration.

2. Theory

(2a) Dimers

Using a conventional molecular field theory approach, we may set up the dimer situation as in Fig. 1 which shows the two spins at angles θ_1 and θ_2 to the applied field direction, while the local anisotropy direction is at an angle α . The exchange coupling is assumed to be antiferromagnetic and hence, for each spin, it will be directed antiparallel to the direction of its neighbour. Writing down the total magnetic energy for each spin we get:

$$E_1 = 2JS^2 \cos(\theta_2 - \theta_1) - g\mu_B BS_1 \cos\theta_1 + K\sin^2(\alpha - \theta_1),$$

$$E_2 = 2JS^2 \cos(\theta_2 - \theta_1) + g\mu_B BS_2 \cos\theta_2 + K \sin^2(\alpha - \theta_2),$$

where J is the exchange constant, K is the anisotropy constant and B is the applied field.

The conventional procedure would then be to differentiate the two equations with respect to the appropriate θ , equate the derivatives to zero and solve them simultaneously for θ_1 and θ_2 for that particular (B, J, K, α) set. However, this leads to two coupled equations which cannot be solved analytically. It is thus necessary to solve the equations numerically and it becomes easier to search for the minima in the sum function for the total energy, taking account of the self-energy, rather than search for the zeroes in the derivatives.

The search for the minimum, for a particular (B, J, K) set, was started by calculating the total energy for (θ_1, θ_2) values in a grid search, using increments of 1° and the position of the minimum estimated. These angle estimates were then used in the IMSL routine DUMING to determine the exact angles at the function minimum. The calculations were repeated for values of α in the range $0 \leq \alpha \leq \pi/2$ in 2° steps. These results, weighted by $\sin\alpha$ as appropriate for a sphere, were used to calculate the average values of θ_1 and θ_2 over the anisotropy directions. The calculations were carried out for values of B , J and K in the ranges:

$$0.1 \leq B \leq 15 \text{ T}, \quad 0.1 \leq J/k_B \leq 100 \text{ K}, \quad 0.01 \leq K/k_B \leq 10 \text{ K}.$$

(2b) Trimers

The trimer was assumed to be a linear, or approximately linear, array with no direct interaction between the end members. It was also assumed that the arrangement is symmetrical about the central atom and that the anisotropy direction is the same for all three atoms. The convention is the same as in Fig. 1 except that both spins 1 and 3 point along the spin 1 direction, so this gives the following free energy equations:

$$E_{1,3} = 2JS^2 \cos(\theta_2 - \theta_1) - g\mu_B BS \cos\theta_1 + K \sin^2(\alpha - \theta_1),$$

$$E_2 = 4JS^2 \cos(\theta_2 - \theta_1) + g\mu_B BS \cos\theta_2 + K \sin^2(\alpha - \theta_2).$$

The analysis for finding the minima in the total energy function, again having halved the self-energy terms, was carried out the same way as for the dimer case and for the same range of interactions.

3. Results

(3a) Dimers

The computer generated minimisations were carried out for values of B , J and K equally spaced on a logarithmic scale. The problem of choosing the best method of presenting such a considerable amount of data is a complex one. For experimentalists, we believe that it is easiest to visualise plots of the data when the applied field is the chief independent variable because this is the one over which we have control. Thus, one technique is to give the data as three-dimensional (3D) plots, for example θ_1 as a $f(B, J)$ for a particular K value. We believe that such plots give the best visualisation for selecting experimental conditions. However, it lacks the accuracy needed for reading off numerical values for the other use, namely evaluating constants from experimental data. This use really requires 2D slices of the 3D graphs which are very space consuming. Accordingly, we have selected out sufficient 3D plots for this paper to cover the range of circumstances. Readers who would like additional data or the complete set can obtain them by downloading either the plots which we have produced (as postscript files) or the complete data with instructions for producing their own plots from our home page at www.monash.edu.au/physics/.

Figs 2–5 show the plots for (a) spin 1 and (b) spin 2 for four different values of the anisotropy constant, as a function of applied field and exchange constant. It was found to be easier to interpret the θ_2 diagrams if they were plotted as $(\pi - \theta_2)$, that is the angle from the positive magnetic field direction as for θ_1 . Thus for spin 1, θ_1 is always in the first quadrant, while for spin 2, positive values of $(\pi - \theta_2)$ are in the second and third quadrants. Some diagrams also have negative values of $(\pi - \theta_2)$, which are in the first quadrant. Thus in Fig. 2, if we consider medium values of J , then initially the spins are antiparallel, with the average direction being approximately at the tetrahedral angle, 57.5° and $(180^\circ - 57.5^\circ)$, from the field direction. Increasing the applied field brings on the spin flop, with both spins being at the same angle (approximately 80 – 90°) on opposite sides of the applied field direction. The field at the onset of the spin flop is proportional to J at constant anisotropy values. Further increase in the applied field causes both spins to rotate together towards the field direction, maintaining their mirror image configuration until saturation is reached. At very low values of J , the spin flop has already been induced by the 0.1 T field at which the simulations commenced.

Increasing the anisotropy value as in Fig. 3, results in the flop region moving to higher applied fields, but without appreciably changing the approach to saturation. In Fig. 4a, the process continues, although the flop is becoming less distinct at low J values since these no longer satisfy the condition that the anisotropy field is much smaller than the exchange field. By Fig. 5a, the flop has been replaced by a smooth rotation over the near half of the diagram.

The plots for θ_2 in this region have also become more complicated. In Figs 4b and 5b it can be seen that the plot splits into two branches above 0.3 T. This is

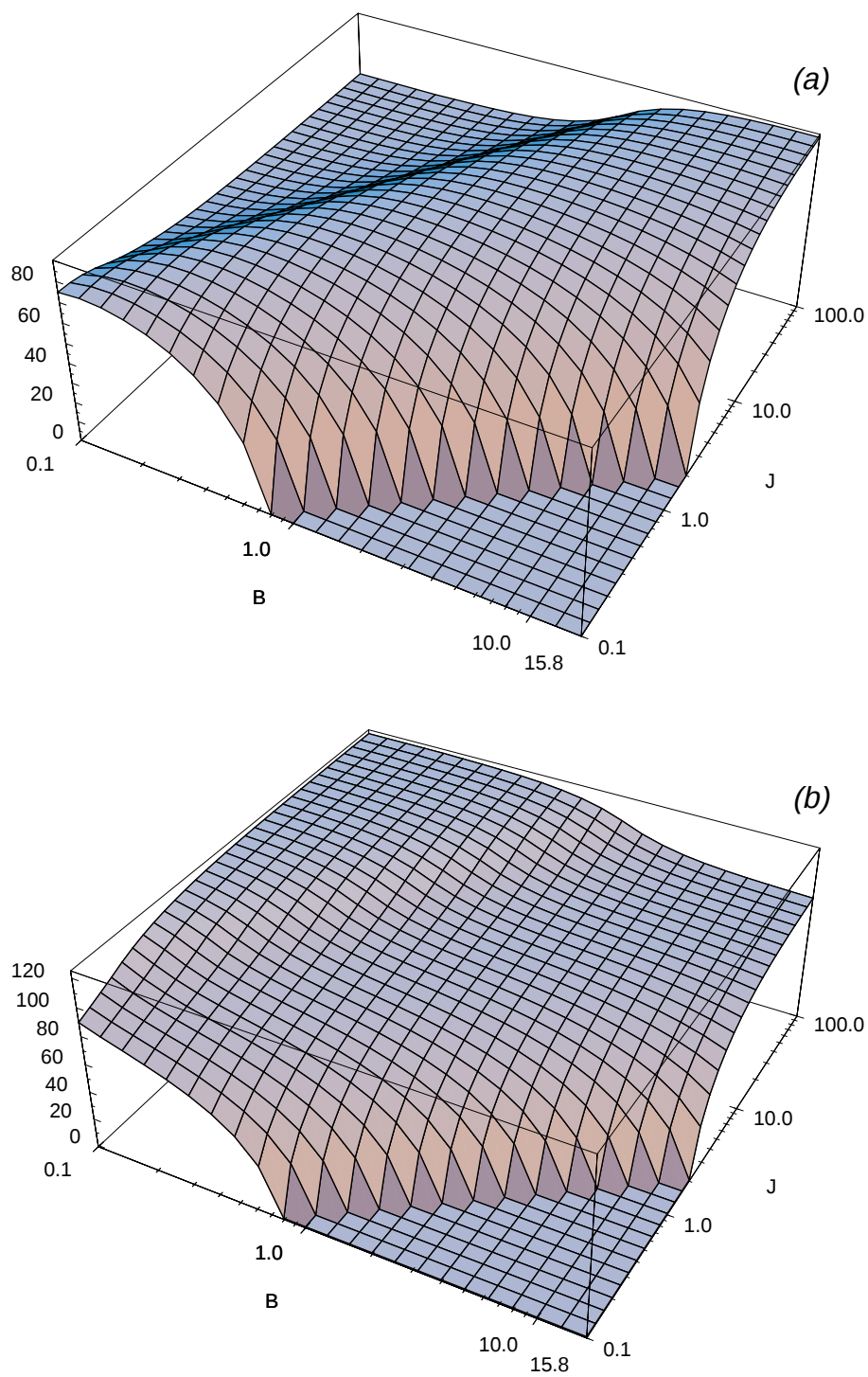


Fig. 2. Angular variation of (a) θ_1 and (b) $(\pi - \theta_2)$ for the dimer configuration and anisotropy constant $K/k_B = 0.01$ K. Note that for Figs 2–10 J is negative and in units of K. The units for B are T.

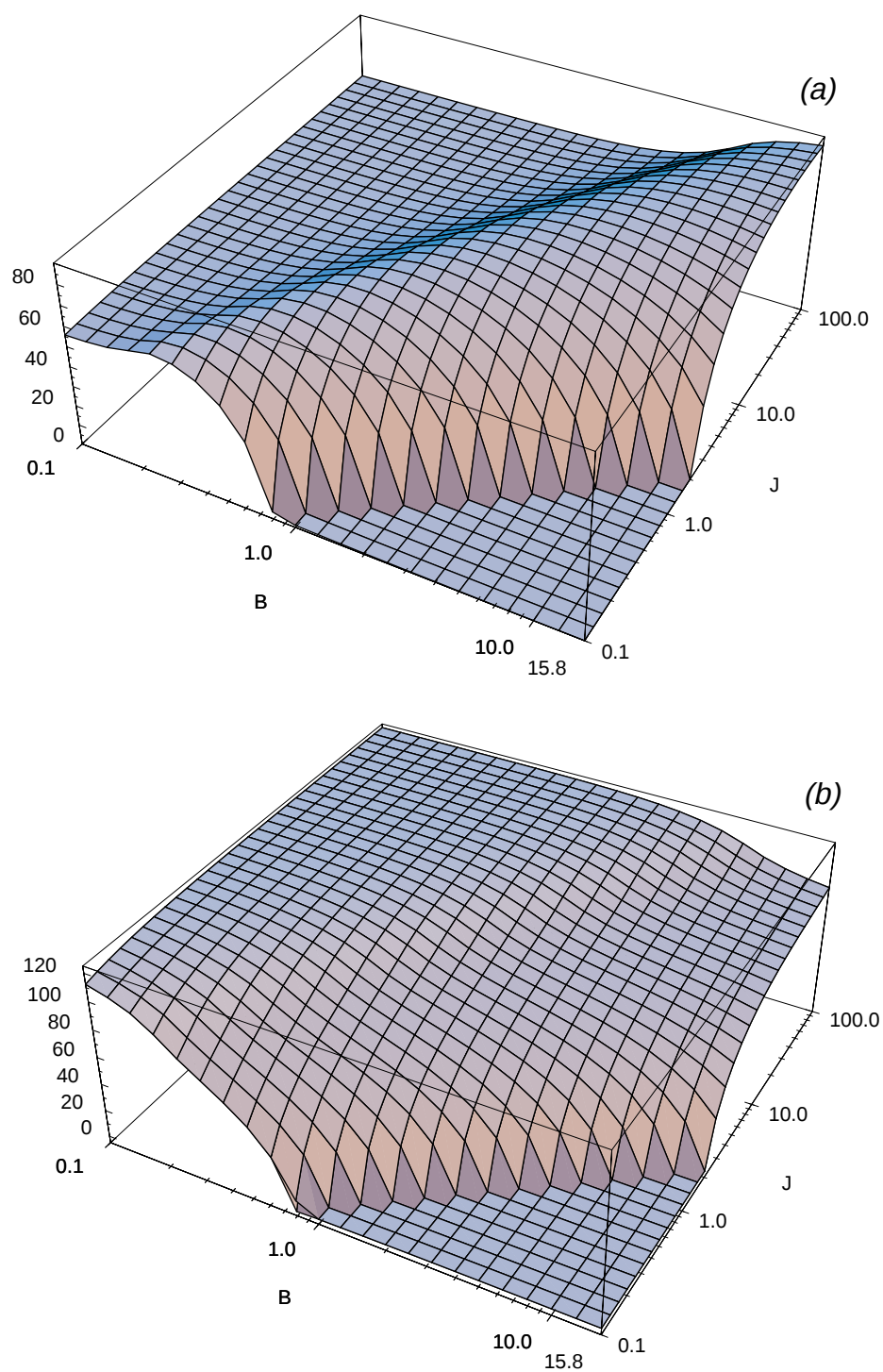


Fig. 3. Angular variation of (a) θ_1 and (b) $(\pi - \theta_2)$ for the dimer configuration and anisotropy constant $K/k_B = 0.1$ K.

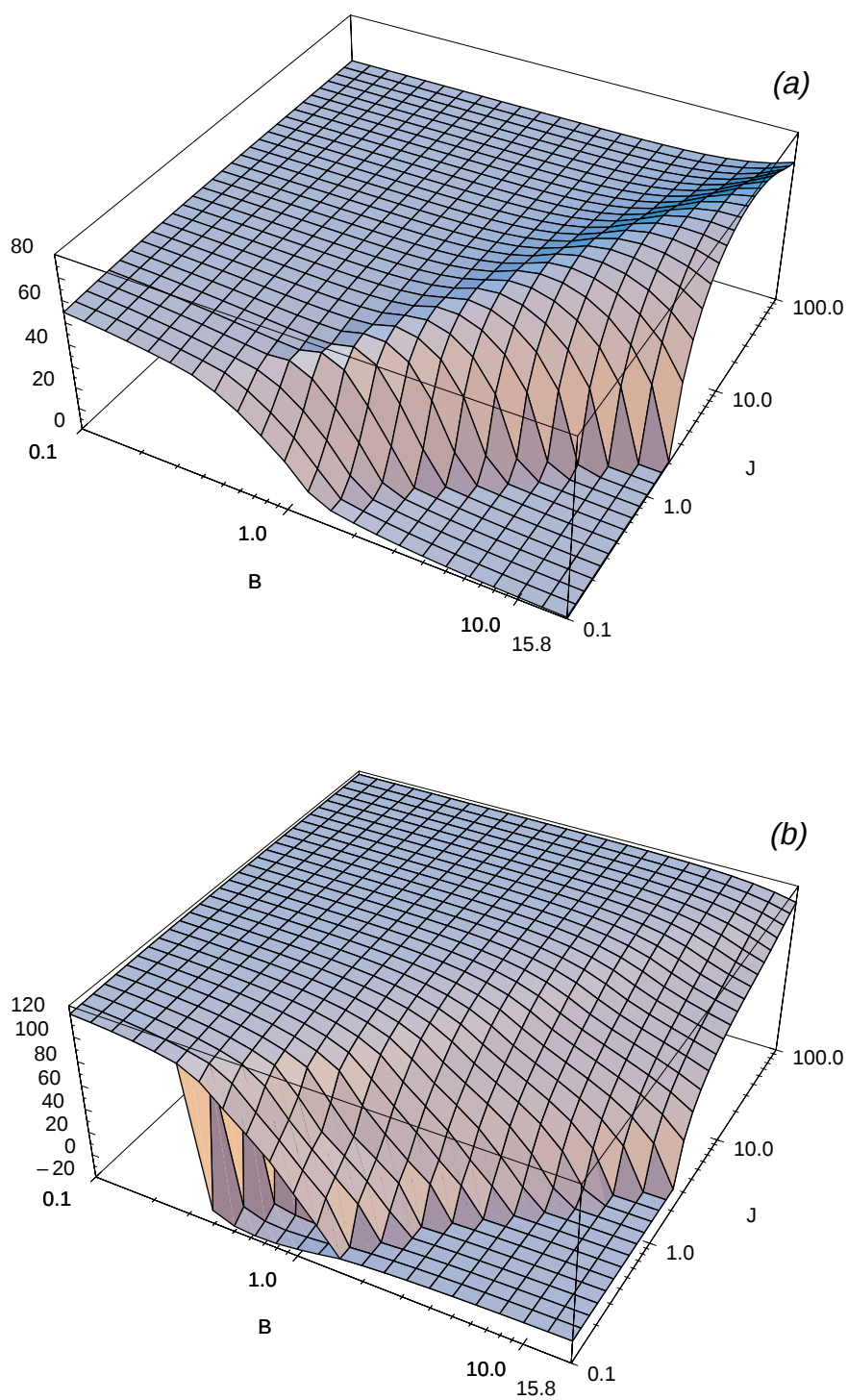


Fig. 4. As for Fig. 3, but for the anisotropy constant $K/k_B = 1.0$ K.

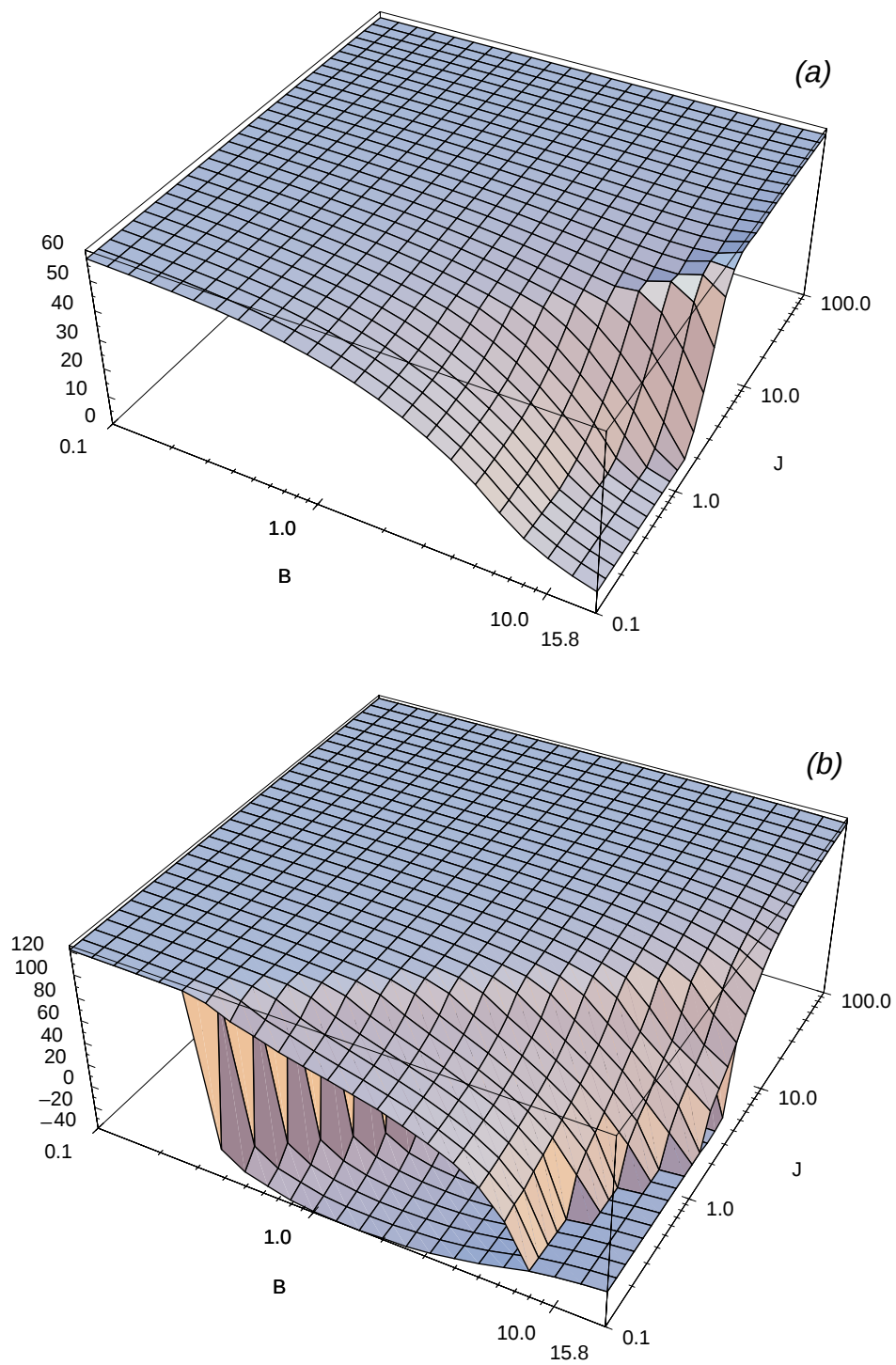


Fig. 5. As for Fig. 3, but for the anisotropy constant $K/k_B = 10$ K.

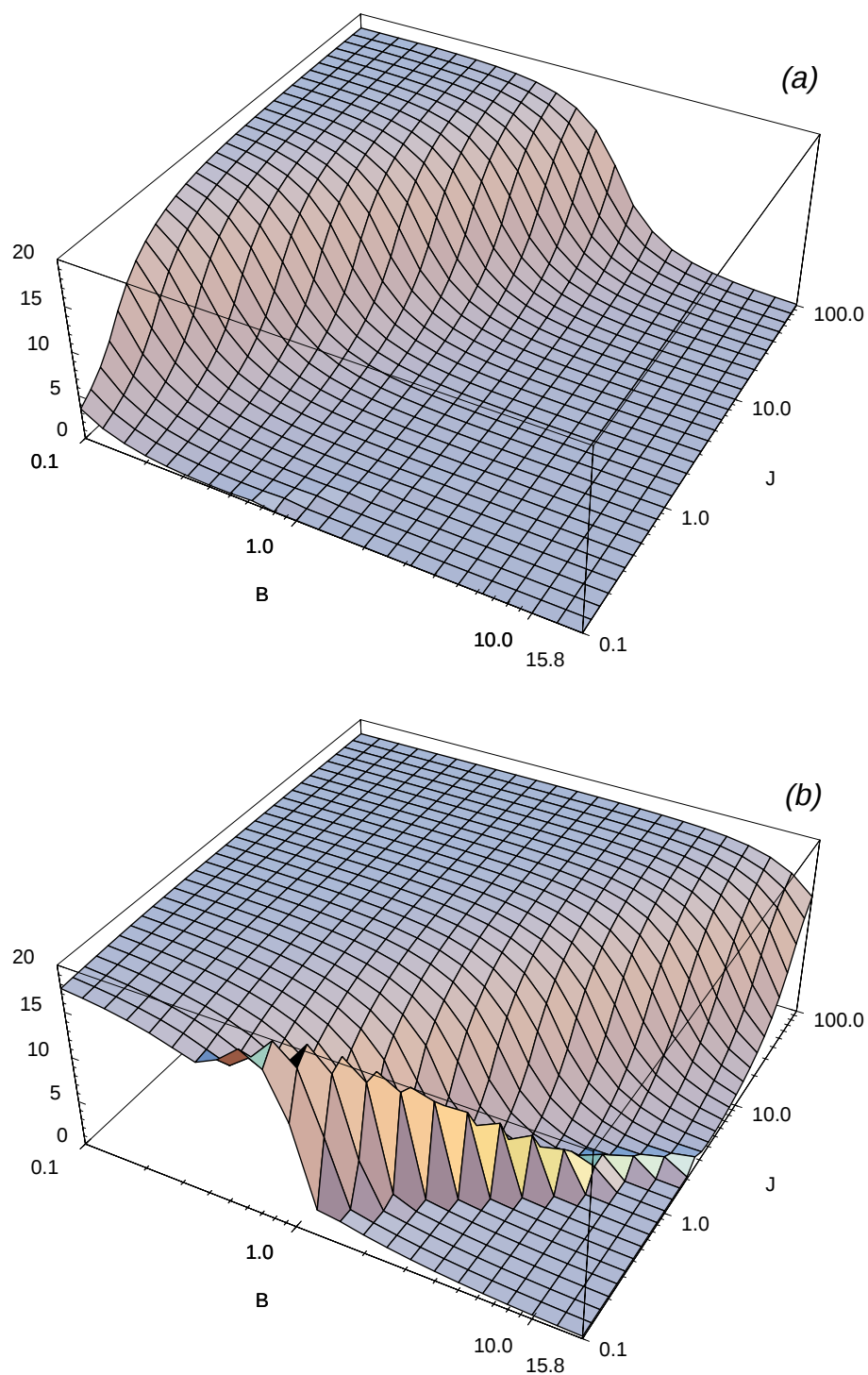


Fig. 6. Angular variation of the standard deviations of θ_1 , for the dimer configuration and anisotropy constant K/k_B equal to (a) 0.01 K and (b) 1 K.

due to the occurrence of a spin flip for spins whose local anisotropy direction is close to the applied field direction, while those spins more perpendicular to the applied field direction undergo a smooth rotation. The proportion of spins in this flip branch increases as the anisotropy constant increases. Both branches should be visible in a high resolution Mössbauer spectrum as two separate sextets.

In the regions where a spin flip or flop is occurring, the first spins to change direction will be those with their local anisotropy direction closest to the magnetic field direction. Both processes will take place over some range of applied field values and there is useful information in the spread of θ values occurring, since this will be observable in the Mössbauer spectrum as a line broadening. As an example of this, Fig. 6a shows the corresponding standard deviations for the θ_1 value in Fig. 2. It can be seen that the standard deviation is initially large and then drops dramatically at the spin flop, remaining low during the rotation to saturation. The variation of the standard deviation for θ_2 is visually identical, in spite of the considerable difference in the angle plots. Fig. 6b shows the standard deviation for the θ_1 value in Fig. 4, where again there is a drop at the spin flop. However, there is now a peak near the approach to saturation because this is no longer an entirely smooth rotation since some of the spins are coupled to spins in the flip branch of θ_1 . The plot for θ_2 shows a very similar structure but is complicated by having two separate standard deviations in one section.

For the high anisotropy plots, the standard deviation in the upper (rotation) branch is much smaller than in the lower (flip) branch. For readers who access the plots from our web page, we note that as a convention for the plotting, the standard deviations for the flip branch have been plotted as negative in order to preserve the structural similarity with the angle plots, although standard deviations strictly cannot be negative.

(3b) Trimers

The trimer case is somewhat simpler to understand because, with the mirror symmetry arrangement relating spins 1 and 3, the magnetic field now has an unbalanced or ferrimagnetic system to operate on. Thus spins 1 and 3 will align closely with the magnetic field very quickly and remain there with increasing field. At some value of the applied field, spin 2 will flip, but there will not be a flop phase for any values of the anisotropy.

Fig. 7 shows the situation for the lowest anisotropy value in which the spins have already aligned parallel and anti-parallel to the field for the lowest values of applied field. At some critical field, the moments start to rotate and the strength of the exchange coupling causes spins 1 and 3 to move away from the applied field direction during the rotation of spin 2 until saturation is achieved. The higher anisotropy value in Fig. 8 shows greater randomisation at low fields, with a correspondingly increased standard deviation. By $K/k_B = 1.0$ K, in Fig. 9, the bulge in the θ_1 contour due to the flip has started to disappear at low values of the exchange constant, while the θ_2 plot now shows two branches for the flip and rotation possibilities. At the highest anisotropy value (Fig. 10) the spin (1, 3) behaviour has become very smooth, while spin 2 has an enhanced branched region. In all cases, the standard deviation for spins 1 and 3 were less than those for spin 2.

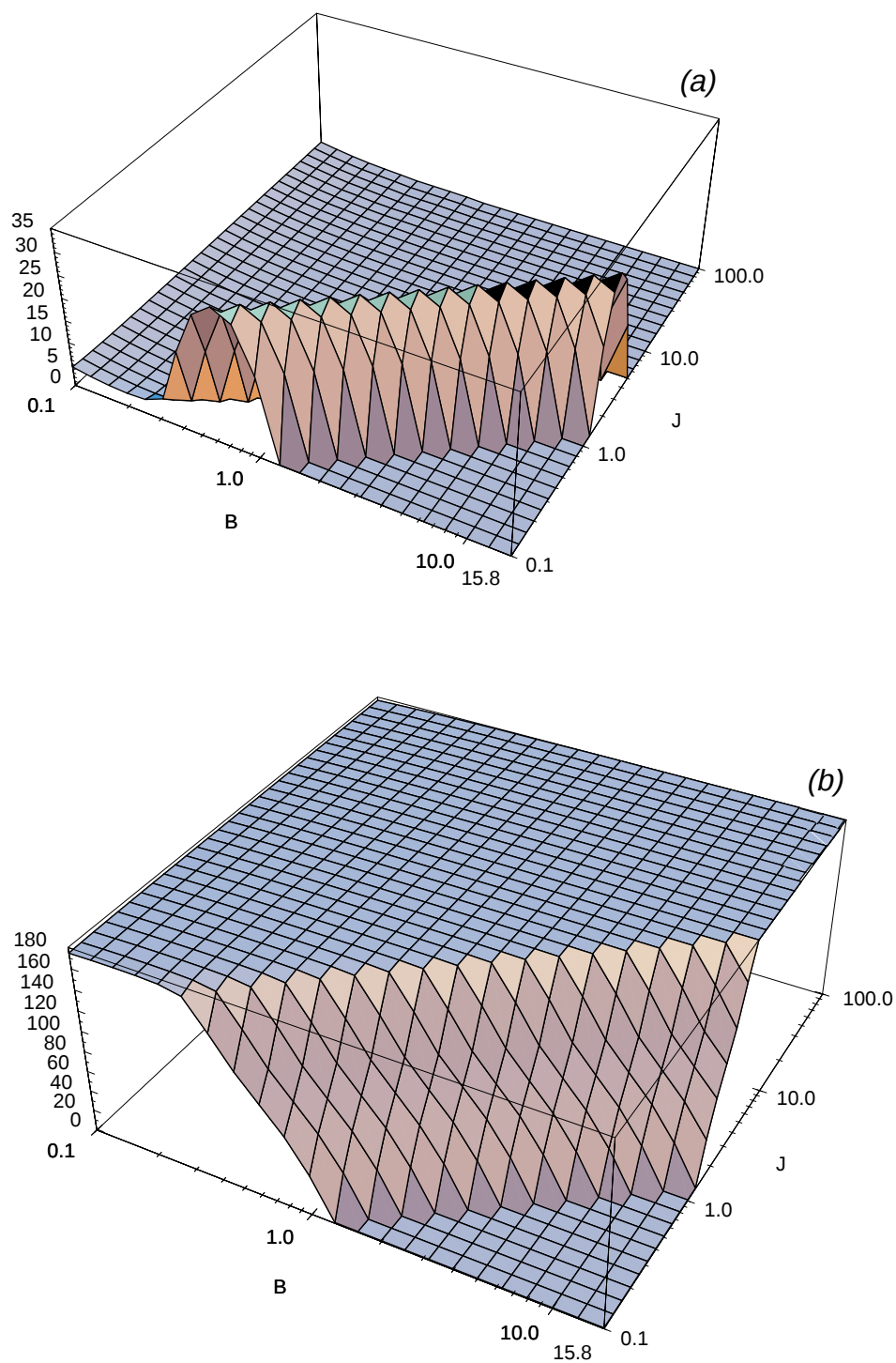


Fig. 7. Angular variation of (a) θ_1 and (b) $(\pi - \theta_2)$ for the trimer configuration and anisotropy constant $K/k_B = 0.01$ K.

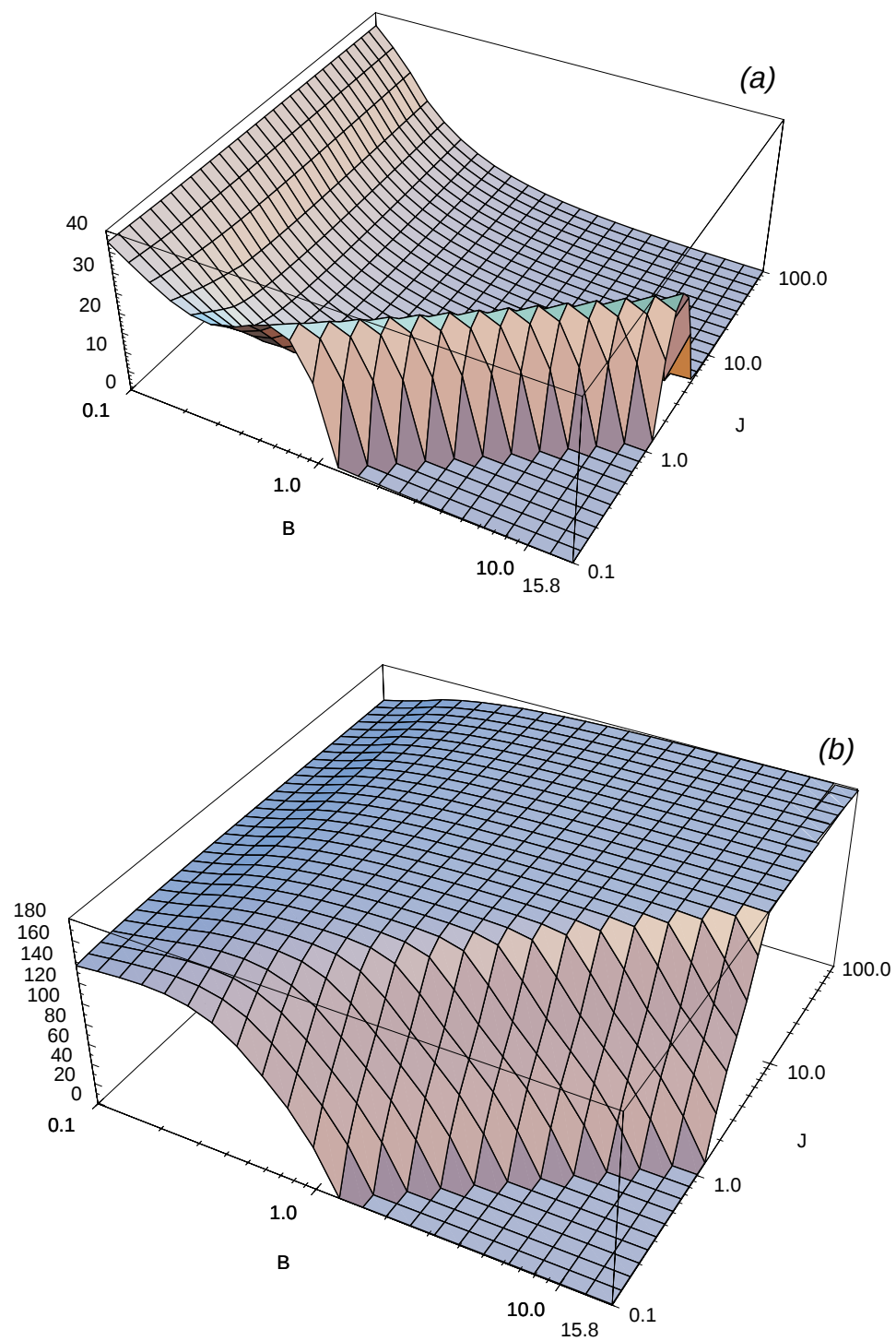


Fig. 8. As for Fig. 7, but for the anisotropy constant $K/k_B = 0.1$ K.

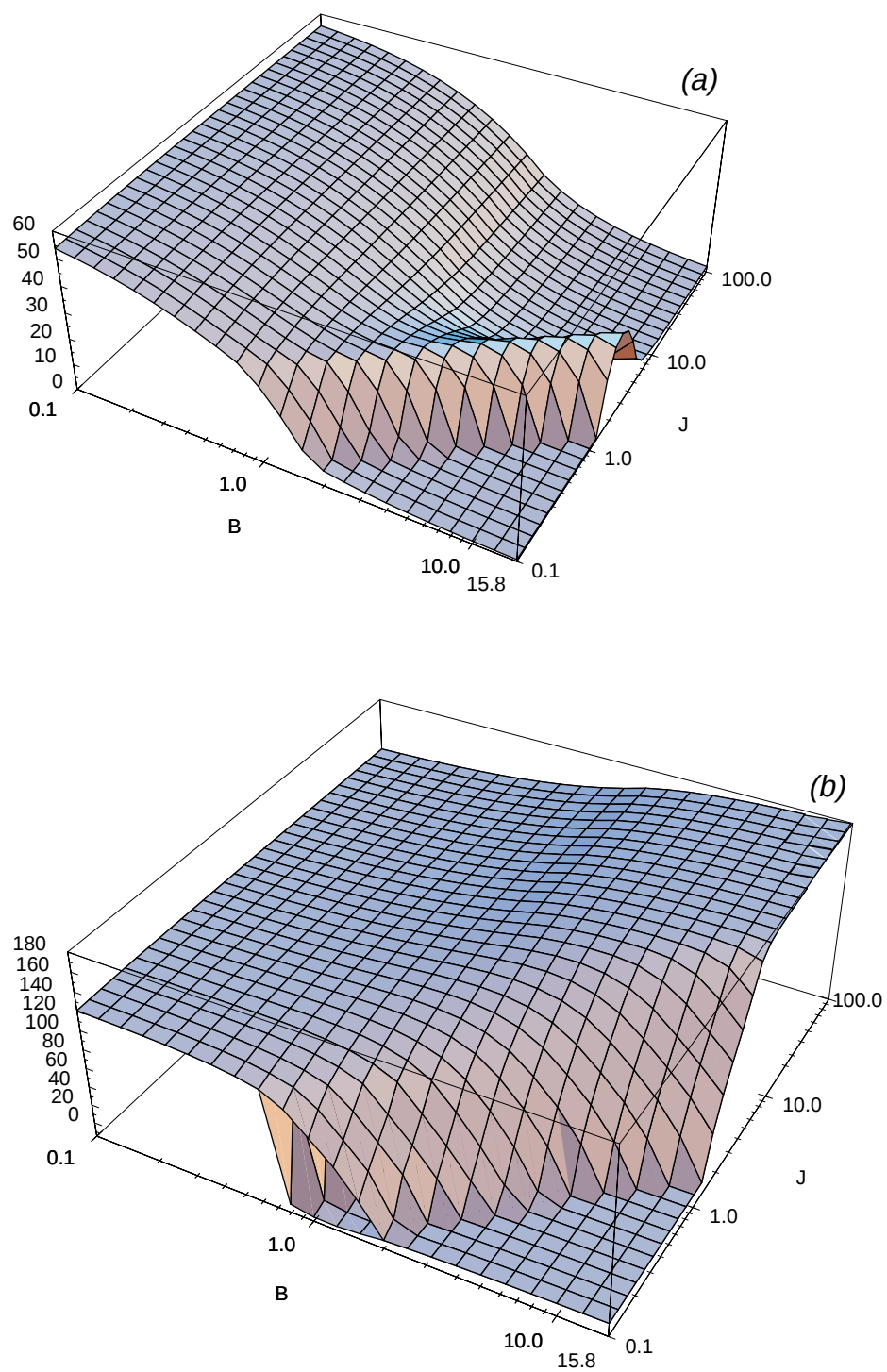


Fig. 9. As for Fig. 7, but for the anisotropy constant $K/k_B = 1.0$ K.

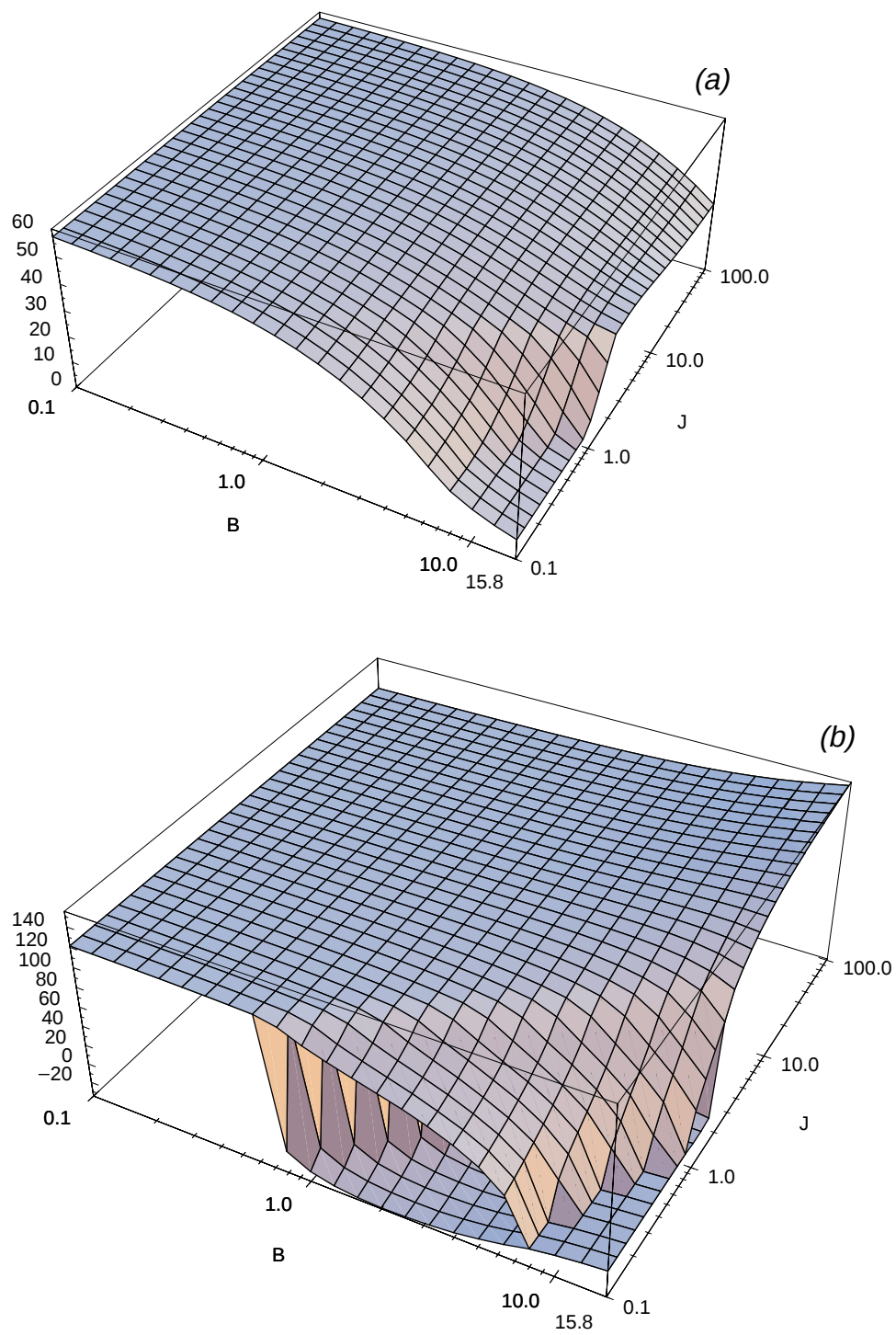


Fig. 10. As for Fig. 7, but for the anisotropy constant $K/k_B = 10$ K.

(3c) Magnetisation

As an additional check, we also computed the magnetisation for each of the arrangements described. These show the expected behaviour of steeply rising contours corresponding to the flop and flip transitions, with the transition region becoming more rounded with an increase in the anisotropy. However, the variation in the plots is small compared to the variations in the angular dependences, emphasising the difficulty of extracting the detailed microscopic parameters from magnetisation measurements.

4. Conclusions

We have evaluated the allowed configurations for ferric spins in both dimer and trimer situations for a range of values of the exchange and anisotropy interactions and of the applied magnetic field. The figures show the main configurations which may be useful for either interpreting Mössbauer data or for selecting the experimental conditions for a proposed set of experiments. More detailed information on the numerical output is available from the authors at the web site as listed in the results section.

Acknowledgments

This work has been supported by the Australian Research Council. We wish to acknowledge helpful discussions with G. R. Hanson and the assistance of L. J. Brown and B. A. McKinnon in the initial stages of the work.

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