# Entropy and Cross-Relaxation in Spin Systems*

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Several examples of cross-relaxation and harmonic cross-relaxation between magnetic resonance transitions, both nuclear and electronic, have recently been reported. In these experiments, the appropriate cross-relaxation rate equations have generally been invoked to predict the results observed. It is pointed out that if the phenomena can be described in thermodynamic terms using the spin temperatures, then the results can be predicted in a simple fashion by maximizing the spin entropy. A simple approximation for the entropy of a multilevel spin system in terms of the population differences $\Delta n_{ij}$ is derived and applied to a typical cross-relaxation problem.

## INTRODUCTION

SEVERAL recent experiments involving cross-relaxation[1,2] or harmonic cross-relaxation in spin systems (both nuclear and electronic) can be described as follows: two or more thermal reservoirs (the magnetic resonance transitions) which have temperatures (the spin temperatures) come into equilibrium via a heat exchange process (the cross-relaxation process). For this description to be valid, the cross-relaxation time must be much less than the spin-lattice relaxation time, and the cross-relaxation process must be one which at least approximately conserves Zeeman energy.

In cross-relaxation experiments, the final equilibrium conditions are usually predicted from the appropriate cross-relaxation rate equations. For multiple-spin processes, these equations become rather complicated. The main point to be made here is that if the thermodynamic description is valid, then it is probably simpler, and perhaps also more elegant, to predict the final equilibrium conditions from the appropriate thermodynamics, i.e., the maximizing of entropy in adiabatic cases. With this approach, the cross-relaxation rate equations need not be known, although the cross-relaxation process involved must always be known.

## ENTROPY OF A MULTILEVEL SPIN SYSTEM

For a system of $N$ spins distributed over $n$ levels, with $n_i$ spins in the $i$th level, the formula for entropy $S$ is[3]

$$S=-kN\sum_i\left(\frac{n_i}{N}\right)\ln\left(\frac{n_i}{N}\right)$$

$$=kN\ln n-kN\sum_i\left(\frac{n_i}{N}\right)\ln\left(\frac{n_i}{N/n}\right).$$

The term $kN\ln n$ is the entropy when all levels are equally populated. In many cases, the level populations are nearly all equal, $n_i\approx N/n$, and it would be useful to have an expression for entropy in terms of the population differences $\Delta n_{ij}\equiv n_i-n_j$ rather than in terms of the actual populations. We will derive such an approximate expression as follows. Let $\delta_i=n_i-N/n$, and shift the zero of entropy by dropping the $kN\ln n$ term. Then, using the approximation for the ln of a number near unity (two terms must be kept) and noting that $\sum\delta_i=0$, we can go through the following derivation:

$$\begin{aligned}S&=-kN\textstyle\sum_i(1/n+\delta_i/N)\ln(1+n\delta_i/N)\\&\approx-\tfrac{1}{2}(k/N)\textstyle\sum_i n\delta_i^2\\&=-\tfrac{1}{2}(k/N)[\textstyle\sum_i(n-1)\delta_i^2-2\sum_{i>j}\delta_i\delta_j]\\&=-\tfrac{1}{2}(k/N)\textstyle\sum_{i>j}(\delta_i-\delta_j)^2\\&=-\tfrac{1}{2}(k/N)\textstyle\sum_{i>j}\Delta n_{ij}^2.\end{aligned}$$

The final line expresses the entropy in terms of the population differences.

## APPLICATION TO A CROSS-RELAXATION EXPERIMENT

A fairly simple example will demonstrate the thermodynamic approach. The cross-relaxation experiment of Sorokin et al. on nitrogen centers in diamond[2] was explained using the multiple-spin cross-relaxation process of Fig. 1, where $a$, $b$, $c$ represent the three allowed magnetic resonance transitions. The entropy is

$$S=-\tfrac{1}{2}(k/N)[\Delta n_a^2+\Delta n_b^2+\Delta n_c^2],$$

and the cross-relaxation process imposes the constraints

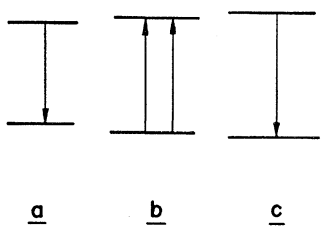


FIG. 1. Multiple-spin cross-relaxation process observed on nitrogen centers in diamond.

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[1] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. 114, 445 (1959).

[2] Cf., papers by P. Sorokin *et al.*; F. R. Nash and E. Rosenvasser; B. Bolger; W. S. C. Chang; and S. Shapiro and N. Bloembergen in *Quantum Electronics*, ed., C. H. Townes (Columbia University Press, New York, 1960).

[3] C. Kittel, *Elementary Statistical Physics* (John Wiley & Sons, Inc., New York, 1958).

$d(\Delta n_a)=d(\Delta n_c)=-\frac{1}{2}d(\Delta n_b)$. Suppose that transition $c$ is saturated by an rf signal, $\Delta n_c \rightarrow 0$. In thermodynamic terms, transition $c$ is placed in thermal contact with a heat source whose temperature is essentially infinite. The spin temperature of $c$ will thereupon be heated to infinity. Transition $c$ is also in heat contact with transitions $a$ and $b$ via the cross-relaxation process. The final equilibrium conditions for $a$ and $b$ must be predicted by maximizing the total entropy, subject to the cross-relaxation constraints.

If $\Delta n_a$ and $\Delta n_b$ have the same initial value $\Delta n_0$, the relationship between them at any time is $\Delta n_b=3\Delta n_0-2\Delta n_a$. The first two terms in the entropy expression can be written with $\Delta n_b$ eliminated as

$$S=-\tfrac{3}{2}(k/N)[5\Delta n_a{}^2-12\Delta n_0\Delta n_a+9\Delta n_0{}^2].$$

Maximizing this expression against $\Delta n_a$ yields

$$\Delta n_a=6/5\Delta n_0, \quad \Delta n_b=\tfrac{3}{5}\Delta n_0.$$

Sorokin et al. predicted this same result from the rate equations. They also experimentally verified the 20% increase in absorption on $a$ and the 40% decrease on $b$ when $c$ was saturated.

An example in which a multilevel spin system with harmonic cross-relaxation between levels is initially perturbed and then allowed to come to equilibrium has also been analyzed by the author, using the same approach. The results show, as one would certainly expect, that the system comes to a new equilibrium in which a Boltzmann distribution prevails among the cross-relaxing levels.


### SUMMARY

An approximate expression for spin-system entropy in terms of the population differences has been given. The expression is useful in finding the final equilibrium conditions in cross-relaxation experiments without needing the cross-relaxation rate equations.


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# Comparison of Structures of Surfaces Prepared in High Vacuum by Cleaving and by Ion Bombardment and Annealing*


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A comparison has been made for a bismuth telluride crystal of the structure of (0001) surfaces produced by cleaving in high vacuum, with similar surfaces prepared by the ion-bombardment and annealing technique. The low-energy electron-diffraction patterns of the two surfaces were found to be similar and of approximately the same intensities. Only integral order beams were present. It is concluded that both methods produce essentially clean surfaces with the same atomic arrangements, in the case of this crystal.


## I. INTRODUCTION

THE method of ion bombardment and annealing developed by Farnsworth et al.,[1] has been extensively used for cleaning surfaces in high vacuum, particularly for nonrefractory substances where heat treatment alone is ineffective. Important evidence that surfaces so produced, under carefully monitored conditions, are atomically clean has been obtained from low-energy electron-diffraction measurements of the cleaned surfaces.[2]

An additional method of producing clean surfaces on bulk single crystals is that of breakage or cleavage in high vacuum. At room temperature the method is obviously more suitable for brittle materials, for example most semiconductors. Comparatively large cleavage faces can be obtained on cleaved and fractured surfaces of various semiconductors.[3] Such surfaces can be assumed to be largely clean if there is negligible contamination from the surrounding low-pressure ambient, or from diffusion of impurities from the uncleaved sides of the specimen. It would be of interest, however, to make measurements, for a particular crystal, on known crystallographic surfaces produced both by cleaving and by ion bombardment and annealing. Since the structures of the surfaces might conceivably be affected by either treatment, low-energy electron-diffraction tests of the surface structures are of particular interest.

Such a comparison has been carried out for bismuth telluride, a semiconductor of rhombohedral structure type $R\bar{3}m$. Regarded as a hexagonal lattice, ready cleavage is observed along (0001) planes, perpendicular to the hexagonal axis. Experiments were made on this material because it cleaves more readily than most semiconductors, a mechanical feature of importance for

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[1] H. E. Farnsworth, R. E. Schlier, M. George, and R. M. Burger, J. Appl. Phys. **26**, 252 (1955).

[2] H. E. Farnsworth, R. E. Schlier, M. George, and R. M. Burger, J. Appl. Phys. **29**, 1150 (1958).

[3] D. Haneman, J. Phys. Chem. Solids **11**, 205 (1959).