PHYSICAL REVIEW VOLUME 98, NUMBER 6 JUNE 15, 1955

Overhauser Nuclear Polarization Effect and Minimum Entropy Production

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(Received February 16, 1955)

This paper gives a simple set of kinetic equations which describe the Overhauser method of producing nuclear polarization by saturating the electronic spin resonance. It is shown that thermodynamically the process consists of absorption of microwave energy and its conversion into heat. In the steady state this process satisfies the principle of minimum entropy production.

I. INTRODUCTION

OVERHAUSER has recently suggested a new method for polarizing nuclei in metals.[1] Overhauser's method requires that the principal mechanism for loss of energy by the nuclear spins be through their coupling to the electronic spins. When this condition is met and when the electronic spin resonance for the conduction electrons is saturated, the population distribution of the nuclear spins among their magnetic levels depends on the magnitude of the electronic magnetic moment rather than on the nuclear magnetic moment. It should therefore be possible to obtain substantial degrees of nuclear polarization under experimentally feasible conditions of temperature and magnetic field strength.[2]

Korringa has shown that Overhauser's method will also work in paramagnetic salts under appropriate circumstances.[3] Kittel has given a simple and general discussion of the Overhauser effect in terms of the general principles of statistical mechanics.[4]

It is the purpose of the present paper to look at the Overhauser effect from still another point of view. When conditions are arranged for producing nuclear polarization, the crystal absorbs microwave energy from an external source and converts this into thermal energy (of conduction electrons or lattice vibrations) in such a way that the population distribution is constant in time. In other words, an irreversible process is occurring and the magnetic system in which it occurs is in a steady state. Under these conditions the behavior of the system should be that required by the principle of minimum entropy production. The discussion which follows is therefore aimed at an added understanding of the Overhauser process from the viewpoint provided by the principle of minimum entropy production.

Before beginning the discussion it seems appropriate to restate the principle. It states that the steady state of a system in which an irreversible process is taking place is that state in which the rate of entropy production has the minimum value consistent with the external constraints which prevent the system from reaching equilibrium. When no such constraints exist the steady state is the equilibrium state in which the rate of entropy production has its absolute minimum, zero. For fuller treatment, the reader is referred to the thermodynamic discussions of the principle by Prigogine[5] and de Groot.[6] A discussion from the viewpoint of statistical mechanics has been given by the author and Meijer, and the present paper is closely related to that discussion.[7]

We must mention that the principle of minimum entropy production is not universally valid. Thermodynamically one can say that it is valid only when the Onsager relations are valid. This essentially requires small deviations from equilibrium. In Sec. III below we shall show the explicit conditions under which the Overhauser process satisfies the principle of minimum entropy production.

II. EQUATIONS FOR THE OVERHAUSER EFFECT

This section is devoted to the formulation of the basic equations for the Overhauser effect. We consider as simple an example as possible in order to emphasize the essential features of the situation.

We consider a nonmetallic crystal containing N nuclear spins, each of magnetic moment $\boldsymbol{\mu}_n$, and N electronic spins, each of magnetic moment $\boldsymbol{\mu}_e$. In an external magnetic field H, the nuclear Zeeman levels are $\pm\mu_n H$ (assuming spin $\hbar/2$). These levels will be denoted by ϵ_1, ϵ_2. The corresponding electronic Zeeman levels $\pm\mu_e H$ will be denoted by ϵ_a, ϵ_b. Let p_1 and p_2 be the probabilities of finding a nucleus in levels ϵ_1 and ϵ_2, and let p_a and p_b be the corresponding probabilities for the electronic levels. The p's are restricted by the two conditions:

$$p_1+p_2=1, \tag{1}$$

$$p_a+p_b=1. \tag{2}$$

We are interested in transitions between these states. It is essential to assume that the nuclei make transitions due only to the interaction with the electron spins, an interaction proportional to $\boldsymbol{\mu}_n\cdot\boldsymbol{\mu}_e$. This interaction will connect only the pairs of states $(1,b)$ and $(2,a)$ since

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* This research was supported by a grant from the National Science Foundation.

[1] A. W. Overhauser, Phys. Rev. **92**, 411 (1953).

[2] T. R. Carver and C. P. Slichter, Phys. Rev. **92**, 212 (1953).

[3] J. Korringa, Phys. Rev. **94**, 1388 (1954).

[4] C. Kittel, Phys. Rev. **95**, 589 (1954).

[5] I. Prigogine, *Etude Thermodynamique des Phénomènes irréversibles* (Editions Desoer, Liège, 1947), Chap. V.

[6] S. R. de Groot, *Thermodynamics of Irreversible Processes* (Interscience Publishers, Inc., New York, 1951), Chap. X.

[7] M. J. Klein and P. H. E. Meijer, Phys. Rev. **96**, 250 (1954).

there are no other nonzero matrix elements. The electron spins can make transitions because of this interaction, but we assume that electronic transitions occur primarily because of electron spin-lattice interactions.[8] In the Overhauser effect the system is irradiated by a microwave field tuned to the electron spin resonance ($\hbar\omega=\epsilon_b-\epsilon_a=2\mu_eH$), and this field is therefore another cause of transitions of the electron spins.

Summing up the preceding discussion, we can write the following equations:

$$dp_1/dt=a_{2a,1b}p_2p_a-a_{1b,2a}p_1p_b, \tag{3}$$

$$dp_a/dt=(a_{ba}+c)p_b-(a_{ab}+c)p_a +a_{1b,2a}p_1p_b-a_{2a,1b}p_2p_a. \tag{4}$$

We need not write equations for dp_2/dt and dp_b/dt since they are the negatives of dp_1/dt and dp_a/dt respectively as required by Eqs. (1) and (2). The terms in Eqs. (3) and (4) can be identified as follows. The coefficient $a_{2a,1b}$ is the probability per unit time of a nuclear transition 2→1 coupled with an electronic transition $a\rightarrow b$, due to the $\boldsymbol{\mu}_n\cdot\boldsymbol{\mu}_e$ interaction. The coefficient a_{ba} is the probability per unit time of an electronic transition $b\rightarrow a$ due to the interaction of the electron with the heat bath of lattice vibrations. Finally, c is the electronic transition probability per unit time for transitions induced by the external microwaves. In each term the change per unit time is proportional to the transition probability and to the probability of occupation of the initial state.

The transition probabilities for the inverse transitions are determined by the following relations:

$$a_{ba}e^{-\epsilon_b/kT}=a_{ab}e^{-\epsilon_a/kT}, \tag{5}$$

$$a_{2a,1b}e^{-(\epsilon_2+\epsilon_a)/kT}=a_{1b,2a}e^{-(\epsilon_1+\epsilon_b)/kT}. \tag{6}$$

These relations follow from the fact that energy differences between initial and final states are made up in each case by energy exchanged with the heat bath at temperature T.[9]

The steady-state solutions of Eqs. (3) and (4), i.e., the solutions with $dp_1/dt=dp_a/dt=0$, can be written down. We obtain

$$p_b/p_a=(a_{ba}e^{-(\epsilon_b-\epsilon_a)/kT}+c)/(a_{ba}+c), \tag{7}$$

$$p_2/p_1=(p_b/p_a)e^{-(\epsilon_2-\epsilon_1)/kT}e^{-(\epsilon_b-\epsilon_a)/kT}. \tag{8}$$

The Overhauser effect follows immediately from these solutions. In the absence of the external microwave radiation, $c=0$, the system comes to equilibrium and $p_b/p_a=e^{-(\epsilon_b-\epsilon_a)/kT}$, $p_2/p_1=e^{-(\epsilon_2-\epsilon_1)/kT}$. The nuclear distribution is determined by the nuclear Boltzmann factor, i.e., the exponential of the ratio of the nuclear energy difference ($2\mu_nH$) to kT. In the case of complete saturation, $c\gg a_{ba}$, the occupations of the electronic Zeeman states approach equality ($p_b/p_a\rightarrow 1$), and the nuclear population ratio is given by

$$p_2/p_1=e^{(\epsilon_b-\epsilon_a)/kT}e^{-(\epsilon_2-\epsilon_1)/kT}.$$

We see that the nuclear distribution is now determined primarily by the *electronic* Boltzmann factor which involves μ_e rather than μ_n (a factor of about 10^3). This is the essence of the Overhauser nuclear polarization method.

III. MINIMUM ENTROPY PRODUCTION

This section is devoted to the calculation of the rate of entropy production in our system and to the proof that the principle of minimum entropy production applies to this process. We may point out at the beginning that the "constraint," which prevents the system of nuclear and electronic spins from reaching thermal equilibrium at the temperature T of the heat bath, consists of the coupling to the "reservoir" of microwave power which continuously feeds energy into the system. When this microwave power is removed, $c=0$, the steady state is the equilibrium state.

The total rate of entropy production, dS/dt, is the sum of the rates of charge of the nuclear spin entropy, dS_n/dt, the electronic spin entropy, dS_e/dt, and the entropy of the heat bath dS_B/dt. Since the radiation is essentially monochromatic it does not contribute to the entropy. Consequently we can write the equation

$$dS/dt=dS_n/dt+dS_e/dt+dS_B/dt. \tag{9}$$

The first two terms in Eq. (9) can be evaluated in a simple way from the following equations for the nuclear and electronic spin entropies,

$$S_n=-Nk(p_1\ln p_1+p_2\ln p_2), \tag{10}$$

$$S_e=-Nk(p_a\ln p_a+p_b\ln p_b). \tag{11}$$

The time derivatives are obtained by using Eqs. (3) and (4).

The time rate of change of the entropy of the heat bath can be obtained by the following argument. Since all energy which enters or leaves the bath does so at temperature T, the rate of change of the bath's entropy is $(1/T)$ times the rate of change of the energy of the nuclear and electronic systems, omitting the energy exchanged by the electrons with the microwave radiation. Consequently we can write the equation

$$dS_B/dt=-(1/T)(dU_n/dt+d'U_e/dt), \tag{12}$$

where the prime on the derivative $d'U_e/dt$ means that the terms just mentioned must be omitted. The internal energies U_n and U_e are given by the equations

$$U_n=N(p_1\epsilon_1+p_2\epsilon_2), \tag{13}$$

$$U_e=N(p_a\epsilon_a+p_b\epsilon_b), \tag{14}$$

and their time derivatives are calculated with the help of Eqs. (3) and (4) omitting the terms proportional to c in Eq. (4).

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[8] A. W. Overhauser, Phys. Rev. **89**, 689 (1953).

[9] See the appendix of reference 7 for a detailed discussion.

Carrying out all of the operations previously indicated, we obtain the following expression for the total rate of entropy production:

$$\frac{dS}{dt}=-Nk\left[\alpha\left(p_2p_a-\frac{\rho}{\sigma}p_1p_b\right)\ln\left(\frac{p_1e^{\epsilon_1/kT}p_be^{\epsilon_b/kT}}{p_2e^{\epsilon_2/kT}p_ae^{\epsilon_a/kT}}\right)\right.$$
$$\left.+\gamma(p_b-\sigma p_a)\ln\frac{p_ae^{\epsilon_a/kT}}{p_be^{\epsilon_b/kT}}+c(p_b-p_a)\ln\frac{p_a}{p_b}\right]. \quad (15)$$

The following abbreviations have been used: $\alpha=a_{2a,\,1b}$, $\gamma=a_{ba}$, $\rho=e^{-(\epsilon_2-\epsilon_1)/kT}$, $\sigma=e^{-(\epsilon_b-\epsilon_a)/kT}$.

In order to verify that the principle of minimum entropy production applies to our problem, we must write down the conditions for a minimum value of dS/dt. The derivatives of dS/dt with respect to p_1, p_2, p_a, and p_b are calculated from Eq. (15). Since the four variables are not all independent, we must introduce two Lagrange multipliers, μ and μ', to allow for the constraints expressed in Eqs. (1) and (2). Carrying out the indicated operations, we obtain the following four equations for dS/dt to be stationary.

$$\mu=Nk\left[\alpha(p_2p_a/p_1-\rho p_b/\sigma)\right.$$
$$\left.+\alpha(\rho p_b/\sigma)\ln\frac{p_2e^{\epsilon_2/kT}p_ae^{\epsilon_a/kT}}{p_1e^{\epsilon_1/kT}p_be^{\epsilon_b/kT}}\right], \quad (16)$$

$$\mu=Nk\left[\alpha(\rho p_1p_b/\sigma p_2-p_a)+\alpha p_a\ln\frac{p_1e^{\epsilon_1/kT}p_be^{\epsilon_b/kT}}{p_2e^{\epsilon_2/kT}p_ae^{\epsilon_a/kT}}\right], \quad (17)$$

$$\mu'=Nk\left[\alpha p_2\ln\frac{p_1e^{\epsilon_1/kT}p_be^{\epsilon_b/kT}}{p_2e^{\epsilon_2/kT}p_ae^{\epsilon_a/kT}}+\alpha\left(\frac{\rho}{\sigma}\frac{p_1p_b}{p_a}-p_2\right)\right.$$
$$+\gamma\sigma\ln\frac{p_be^{\epsilon_b/kT}}{p_ae^{\epsilon_a/kT}}+\gamma\left(\frac{p_b}{p_a}-\sigma\right)$$
$$\left.+c\left(\frac{p_b}{p_a}-1+\ln\frac{p_b}{p_a}\right)\right], \quad (18)$$

$$\mu'=Nk\left[\frac{\alpha\rho}{\sigma}p_1\ln\frac{p_2e^{\epsilon_2/kT}p_ae^{\epsilon_a/kT}}{p_1e^{\epsilon_1/kT}p_be^{\epsilon_b/kT}}+\alpha\left(\frac{p_2p_a}{p_b}-\frac{\rho}{\sigma}p_1\right)\right.$$
$$+\gamma\ln\frac{p_ae^{\epsilon_a/kT}}{p_be^{\epsilon_b/kT}}+\gamma\left(\sigma\frac{p_a}{p_b}-1\right)$$
$$\left.+c\left(\frac{p_a}{p_b}-1+\ln(p_a/p_b)\right)\right]. \quad (19)$$

In order to complete the proof it is necessary to introduce the assumption that both p_b/p_a and $p_b/\sigma p_a$ differ from unity by small quantities, quantities whose square may be neglected. This assumption means that the electronic spin system must be close to being equally distributed between states a and b ($p_b \cong p_a$), and also that the Boltzmann factor $\sigma(=e^{-2\mu_eH/kT})$ must be close to unity. This last remark implies that at low temperatures and in strong fields, where the Overhauser effect is experimentally most likely to be important, the principle of minimum entropy production will not be satisfied. The Overhauser effect will of course exist under those conditions, but the steady state will not be the state of minimum entropy production.

When the assumption discussed in the preceding paragraph is valid it can be shown in a straightforward way that the steady state is the state of minimum entropy production. More precisely, it can be shown that (a) if there is a steady state, then Eqs. (16)–(19) for stationary dS/dt are satisfied with $\mu=\mu'=0$, and (b) if Eqs. (16)–(19) for stationary dS/dt are satisfied, then $\mu=\mu'=0$ and p_1, p_2, p_a, and p_b are constant in time.[10]

The final point to be established is that the stationary value of dS/dt in the steady state is actually a minimum. This results from a calculation of the deviation $\delta(dS/dt)$ from its value in the steady state. If p_i^0 are the steady-state values and δp_i their deviations, then direct algebraic manipulation leads to the result

$$\delta\left(\frac{dS}{dt}\right)=Nk\left\{\frac{\gamma+c}{p_a^0}\left[\left(\frac{p_b^0}{p_a^0}\right)^{\frac{1}{2}}\delta p_a-\left(\frac{p_a^0}{p_b^0}\right)^{\frac{1}{2}}\delta p_b\right]^2\right.$$
$$+\alpha\left[\frac{(p_2^0p_a^0)^{\frac{1}{2}}}{p_1^0}\delta p_1-\left(\frac{p_a^0}{p_2^0}\right)^{\frac{1}{2}}\delta p_2\right.$$
$$\left.\left.-\left(\frac{p_2^0}{p_a^0}\right)^{\frac{1}{2}}\delta p_a+\frac{(p_2^0p_a^0)^{\frac{1}{2}}}{p_b^0}\delta p_b\right]^2\right\}, \quad (20)$$

and this sum of squares is positive, implying that dS/dt is indeed a minimum in the steady state.

IV. DISCUSSION

The form of the entropy production in the steady state is of some interest as it lends itself to a direct physical interpretation. In the steady state the first two terms of Eq. (9) vanish and so does the first term in Eq. (12) because all these terms involve derivatives of the p_i. The only remaining contribution to the entropy production in the steady state is $-(1/T)(d'U_e/dt)$. We can therefore write

$$(dS/dt)_{\min}=-(N/T)\{(\gamma p_b-\gamma\sigma p_a)(\epsilon_a-\epsilon_b)\}, \quad (21)$$

and using the fact that $(dp_a/dt)=(dp_b/dt)=0$ this can be reduced with the help of Eq. (4). Our final expression is

$$(dS/dt)_{\min}=\{(\epsilon_b-\epsilon_a)/T\}Nc(p_a-p_b). \quad (22)$$

In other words entropy is produced in the steady state by transforming the quanta absorbed from the microwave radiation into thermal energy at tempera-

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[10] The details of the proof are similar to those in reference 7, Sec. IV. See also J. S. Thomsen, Phys. Rev. **91**, 1263 (1953), Sec. III; M. J. Klein, Phys. Rev. **97**, 1446 (1955).

ture T. The first factor $(\epsilon_b-\epsilon_a)/T$ is the entropy increase for each quantum so transformed, and the second factor $Nc(p_a-p_b)$ is the net number of quanta absorbed per unit time.

In conclusion we may say that the viewpoint of irreversible thermodynamics and the principle of minimum entropy production provide additional insight into the nature of the Overhauser nuclear polarization effect.

ACKNOWLEDGMENTS

The author would like to express his thanks to Professor Jan Korringa of the Ohio State University for two helpful discussions.

PHYSICAL REVIEW VOLUME 98, NUMBER 6 JUNE 15, 1955

Work Function of Cadmium*

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(Received March 1, 1955)

The contact difference of potential Cd-Ba is measured by the electron beam and Kelvin methods. These measurements agree within the limits of reproducibility of either method alone and yield a work function value of 4.08±0.02 ev for the work function of cadmium films deposited on tantalum. The barium surfaces, formed by redistillation following fractional distillation, show their characteristic constancy and reproducibility to ±0.01 ev. Cadmium retains some gas after exhaustive multiple distillation. Measurements taken immediately after deposition of a Cd film and during its aging show (1) that freshly deposited Cd films are generally contaminated with gas which distills with the metal; (2) that the adsorbed gas is removed progressively by getter clean-up with an attendant rise in work function totalling 0.10 ev in extreme cases, and (3) that the work function thus established is constant and reproducible to 0.03 ev or better. Comparison of these measurements with our earlier work on zinc leads to the conclusion that a cadmium surface in equilibrium with the residual gas of a well-gettered tube contains so little adsorbed gas that its final work function can probably be accepted as characteristic of the clean metal.

THIS report describes further results in a program in which the external work functions of the pure metals are determined by measurement of their contact differences of potential with respect to a reference metal of known work function, barium. Earlier work in this laboratory[1] has shown that the work functions of zinc surfaces prepared by distillation of the outgassed metal in sealed-off, barium gettered tubes are highly reproducible and constant over long periods of time. Objective evidence for the absence of gaseous contamination was obtained by making the time interval between deposition and measurement of the surfaces short with respect to the time required for deposition of a monolayer of adsorbed gas. A series of similar measurements was carried out on cadmium in 1941 but was not reported at that time. A second series of measurements by a Kelvin technique[2] was completed recently. The results of the two series agree well and taken together constitute a reasonably thorough study of this metal. Since the experimental procedures follow closely those previously described,[1,2] only the variations in technique made necessary by the peculiarities of cadmium are emphasized here. The cadmium employed in these measurements was kindly supplied to me by the New Jersey Zinc Company with an analysis showing a total impurity content of less than 0.001 percent.

ELECTRON BEAM MEASUREMENTS

The high vapor pressure of cadmium at and below its melting point precludes satisfactory outgassing by the method of repetitive fusion commonly used in our work. A second troublesome property of cadmium is its extraordinarily low critical condensation temperature on glass; at room temperature surface migration is so pronounced that agglomeration of the condensate into isolated islands generally occurs. To meet these conditions, tubes of the type used in the measurements on zinc were modified as follows. (1) The multiple distilling arrangement shown in Fig. 1 was substituted for the "first and second vaporizers" of the zinc tubes, and (2) the targets on which the films were formed and measured were 10-mil tantalum foil disks; a 60-mil tungsten post and 60-mil tantalum crossbar replaced the glass target mount of the zinc tubes.

Before charging with cadmium and zinc, the tube was subjected to our standardized outgassing schedule.[1] After charging, the baking temperature was limited to 120°C to avoid vaporization of cadmium. While the tube was on the pumps, fusions of the barium and complete distillations of the cadmium were carried out alternately through ten complete cycles. After seal-off the fusions and distillations were continued until the

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* This research was supported in whole or in part by the U. S. Air Force under a contract monitored by the Office of Scientific Research, Air Research and Development Command.

[1] P. A. Anderson, Phys. Rev. **57**, 122 (1940).

[2] P. A. Anderson, Phys. Rev. **88**, 655 (1952).