

01 Jan 1971

## Activation Volumes Of Interstitial Diffusion In Ferromagnetic Metals And Alloys

Manfred Wuttig

*Missouri University of Science and Technology*

J. Keiser

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### Recommended Citation

M. Wuttig and J. Keiser, "Activation Volumes Of Interstitial Diffusion In Ferromagnetic Metals And Alloys," *Physical Review B*, vol. 3, no. 3, pp. 815 - 821, American Physical Society, Jan 1971.

The definitive version is available at <https://doi.org/10.1103/PhysRevB.3.815>

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Further valuable information could be obtained from measurements in considerably higher fields.

#### ACKNOWLEDGMENTS

We are very obliged to Dr. S. Strässler for many stimulating discussions and to Professor E. E.

Anderson for correspondence concerning his molecular-field calculations for GdIG. We are also indebted to W. Hinz for skillful technical assistance and to A. Beck who grew the GdIG crystal. The critical reading of the manuscript by Dr. C. Schüller and Dr. A. J. Perry is appreciated.

<sup>1</sup>Arthur E. Clark and Earl Callen, *J. Appl. Phys.* **39**, 5972 (1968). A number of references to earlier work are compiled therein.

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<sup>4</sup>A. E. Clark and R. S. Alben, *J. Appl. Phys.* **41**, 1195 (1970).

<sup>5</sup>G. P. Rodrigue, H. Meyer, and R. V. Jones, *J. Appl. Phys.* **31**, 376S (1960).

<sup>6</sup>In garnets containing non-S-state rare-earth ions, the crystal-field interactions at low temperatures cause a decomposition of the rare-earth sublattice and a tilting of the moments, as described, for instance, in S. J. Pickart, H. A. Alperin, and A. E. Clark, *J. Appl. Phys.* **41**, 1192 (1970).

<sup>7</sup>E. E. Anderson, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 660.

<sup>8</sup>Anderson obtained the coefficients by fitting the mag-

netization curve. Due to an error in the nearest-neighbor numbers ( $z_{23}=2$ , and not 4), however, his values are not symmetric ( $\lambda_{23}=2\lambda_{32}$ ). This error already occurs in Pauthenet's paper [R. Pauthenet, *Ann. Phys. (Paris)* **3**, 424 (1958)], while the correct nearest-neighbor numbers can, e.g., be found in a paper by Nowik [I. Nowik, *Phys. Rev.* **171**, 550 (1968)]. We choose  $\lambda_{23}=\lambda_{32}=-4075$  and compensate the so-caused shift of the compensation temperature by changing  $\lambda_{13}$  from  $-800$  to  $-900$ . The corrected set still provides a very good fit for the total and the sublattice magnetizations given in a paper by Myers *et al.* [S. M. Myers, R. Gonano, and H. Meyer, *Phys. Rev.* **170**, 513 (1968)].

<sup>9</sup>The indices 1, 2, and 3 now denote the *a*, *d*, and *c* sites, respectively.

<sup>10</sup>W. A. Crossley, R. W. Cooper, J. L. Page, and R. P. van Stapele, *Phys. Rev.* **181**, 896 (1969).

<sup>11</sup>B. Johnson, *Brit. J. Appl. Phys.* **17**, 1441 (1966); R. R. Alfano and D. H. Baird, *Appl. Phys. Letters* **8**, 338 (1966).

<sup>12</sup>H. Wenking, *Z. Instrumenten K.* **66**, 1 (1958); H. Cary, R. C. Hawes, P. B. Hooper, J. J. Duffield, and K. P. George, *Appl. Opt.* **3**, 329 (1964).

## Activation Volumes of Interstitial Diffusion in Ferromagnetic Metals and Alloys\*

M. Wuttig and J. Keiser

*Department of Metallurgical Engineering, University of Missouri, Rolla, Missouri 65401*

(Received 26 October 1970)

The disaccommodation technique was used to determine the activation volumes of carbon diffusion  $\Delta V$  of a Fe-1.4 wt% Si alloy, of hcp cobalt, and of nickel at the temperatures of  $-21$ ,  $75$ , and  $110^\circ\text{C}$ , respectively. The obtained values of  $\Delta V$  are  $+0.3 \pm 0.3$  and  $-0.6 \pm 0.9 \text{ cm}^3 \text{ mole}^{-1}$  for the two relaxations observed in the Fe-Si alloy,  $-1.7 \pm 2.0$  and  $-0.5 \pm 0.2 \text{ cm}^3 \text{ mole}^{-1}$  for the two relaxations observed in hcp cobalt, and  $1.2 \pm 0.1 \text{ cm}^3 \text{ mole}^{-1}$  for nickel. These results are discussed in terms of a continuum model that interprets the activation energy of diffusion as a sum of the strain and exchange energies. It is found that in ferromagnetic solids the activation volume of diffusion is essentially controlled by the ferromagnetic anharmonicity.

### I. INTRODUCTION

The activation volume of diffusion  $\Delta V$  is the volume change of a crystal that occurs as the diffusing species performs one elementary diffusive jump. In the case of substitutional and self-diffusion,  $\Delta V$  is the sum of the activation volumes of formation  $\Delta V_f$  and migration  $\Delta V_m$ , whereas  $\Delta V = \Delta V_m$  for impurity interstitial diffusion and diffusion by an exchange-type mechanism. On the

basis of a hard-sphere model,<sup>1</sup>  $\Delta V$  would be expected to be positive and of the order of the atomic volume of the diffusing species  $\Omega$ . While negative activation volumes are inconsistent with the hard-sphere model, it is conceivable that  $\Delta V_f < 0$  for vacancy-type defects if the lattice relaxation around the defect is sufficiently large.<sup>1</sup> The activation volume of migration, on the other hand, should not be negative, as this would require that an inward relaxation is associated with the elementary dif-

fusive jump. There is, however, one case where a negative, although very small, activation volume of migration has been observed, namely, for  $N$  diffusion in  $\alpha$ -Fe at  $-20^\circ\text{C}$ .<sup>2</sup> In addition,  $\Delta V_m$  for C diffusion in  $\alpha$ -Fe in the same temperature range is essentially zero<sup>2,3</sup> which is equally incompatible with the hard-sphere model.

In scanning the available data on the pressure dependence of diffusion, it can be seen that the two specific cases mentioned are the only ones deviating grossly from the rule  $\Delta V \approx \Omega$ . It is also seen that these are the only two cases pertaining to a ferromagnetic solid. In order to determine whether or not this latter fact is significant, the pressure dependence of interstitial diffusion in other ferromagnetic solids was investigated. Most activation volumes obtained are in disagreement with the rule  $\Delta V_m \approx \Omega$ ; some are negative. These results will be interpreted in terms of a continuum magnetic energy model, which is an analog of the known continuum strain-energy model.<sup>4</sup>

## II. EXPERIMENTAL TECHNIQUES

The compositions of the alloys investigated are given in Table I. Details on the preparation of the alloys can be found in the references given in this table. The samples were prepared by suitably carburizing high-purity starting materials. All samples investigated were cylindrically shaped and about 0.1 in. diam and  $1\frac{1}{2}$  in. long.

The pressure dependence of the carbon diffusivity was investigated by measuring the relaxation time of the defect redistribution. This time was determined by the disaccommodation technique. Disaccommodation is the effect of a decrease of the initial permeability of a ferromagnetic material following demagnetization. This technique is equivalent to the well-known anelastic technique for the study of point defects. The difference is that in the course of an anelastic experiment the defects redistribute with respect to the applied stress field whereas they redistribute with respect to the intrinsic magnetic field as the disaccommodation proceeds. Further information on the disaccommodation phenomenon in general can be found in a suitable monograph.<sup>8</sup> The specific disaccommodations due to carbon redistribution in Ni,<sup>7</sup> hcp Co,<sup>6</sup> and  $\alpha$ -Fe-Si<sup>5</sup> have been described elsewhere.

The centerpiece of the apparatus consisted of a

conventional Cu-Be high-pressure vessel<sup>9</sup> which housed the solenoid used to determine the initial permeability of the samples. The design pressure of the vessel was 10 kbar. A mixture of one part kerosene and two parts Diala AX oil was used as a pressure transmitting fluid. Electrical and thermocouple feedthroughs were made by brazing No. 30 sheathed wires to the Cu-Be closure plug.<sup>10</sup> For heating, No. 16 Nichrome-V sheathed wire was incorporated into the Cu-Be pressure vessel. These heaters were arranged in such a way that the magnitude of the dc magnetic field attending the heating current was minimized. In conjunction with the magnetic shielding placed directly around the solenoid to reduce the earth's magnetic field, this arrangement of the heaters resulted in residual dc magnetic fields of less than 1.5 mOe at the location of the sample.

Tight pressure and temperature controls were required to determine the small-pressure dependence of the relaxation times with reasonable precision. Standard control equipment employing thermocouple sensors was used to heat the Cu-Be vessel to the desired temperature and maintain this temperature. In order to maintain temperatures below ambient, the vessel was placed in a freezer and backheated by the temperature controller. The sample temperature itself was determined by a Cu-Constantan thermocouple located inside the Cu-Be high-pressure vessel. At this position, the temperature was kept constant to  $\pm 0.02^\circ\text{C}$  for temperatures above and  $\pm 0.04^\circ\text{C}$  for temperatures below ambient. The pressure-generating equipment consisted of a commercially available pump and intensifier. An aged manganin resistor housed in a separate vessel was used as a pressure gauge. The resistance of the gauge was determined by a Wheatstone bridge, the output of which was fed in a controller which operated a pressure transducer. This transducer in turn regulated the air pressure driving the primary pump. In this way, a pressure could be "dialed" and controlled by selecting a suitable combination of reference resistors of the Wheatstone bridge. The solid-liquid transformation of mercury was used for the calibration of the manganin gauge.<sup>11</sup> An analysis of the calibration procedure yielded an accuracy of the pressure readings of better than 4.1%. Using this control equipment, the pressure was kept constant to better than  $\pm 4$  bar up to pressures of 6 kbar.

## III. RESULTS

The results of this study are presented in Figs. 1-4 and in Table II. A typical plot of the time dependence of the inverse of the initial permeability, the reluctivity  $r$ , of the Ni-C alloy measured at  $110^\circ\text{C}$  is shown in Fig. 1. In this figure both co-

TABLE I. Carbon contents of investigated alloys.

Alloy	Carbon content (wt%)	Ref.
Fe-1.4 wt% Si-C	0.003	5
hcp Co-C	0.37	6
Ni-C	0.31	7

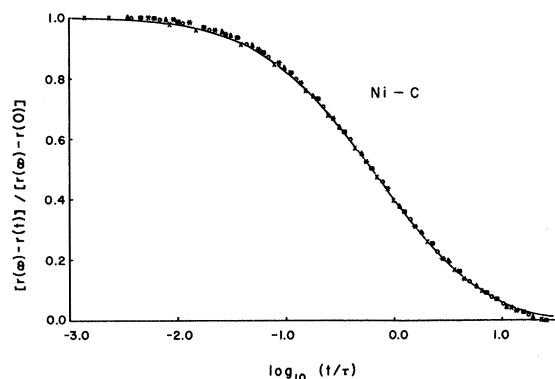


FIG. 1. Normalized reactivity as a function of the logarithm of the normalized time of a Ni-0.31 wt% C alloy measured at 110 °C at various pressures. Definition of symbols: squares, ambient pressure; circles, 0.94 kbar; exes, 1.87 kbar; triangles, 2.83 kbar; stars, 3.74 kbar.

ordinates are normalized so that the data taken at all pressures can be compared to one master curve. This master curve was calculated by using average values for the relaxation amplitude and half-width. The relaxation amplitudes  $[r(\infty) - r(0)]$ , and times  $\tau$ , as well as the half-widths  $\beta$ , of the assumed

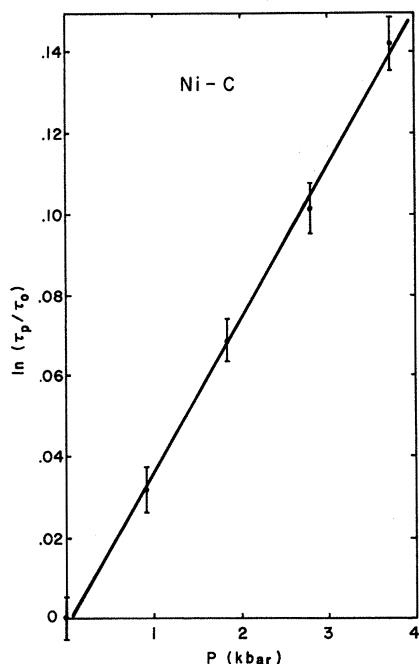


FIG. 2. Pressure dependence of the relaxation time of carbon redistribution in a Ni-0.31 wt% C alloy measured at 110 °C.  $\tau_p$  is the relaxation time at pressure  $p$  and  $\tau_0$  the relaxation time at ambient pressure.

Gaussian distribution of the relaxation times were obtained from a least-squares analysis of the disaccommodation data in terms of a sum of exponentials. This procedure has been described elsewhere.<sup>6</sup> In essence, it consisted of an iterative minimization of the linearized variance. It can be seen from Fig. 1 that the master curve represents the data points satisfactorily.

The relaxation times obtained in the manner described and normalized to the time observed at ambient pressure are plotted semilogarithmically in Figs. 2-4 as a function of pressure for the three alloys investigated. The subscripts 1 and 2 on the ordinates of Figs. 3 and 4 refer to the short and long time components of the disaccommodations, respectively. In the case of the Fe-Si-C alloy, the short time component is due to the redistribution of carbon interstitials having only iron nearest neighbors, whereas the long time component is due to the redistribution of interstitials having also Si neighbors.<sup>5</sup> The modes of redistribution in the hcp Co-C alloy are not known.<sup>6</sup> The error limits represent the 95% confidence limits of the least-squares analysis. The temperature varied from run to run by as much as 0.1 °C. Therefore, all relaxation times presented in Figs. 2-4 were reduced to the temperatures at which the run at ambient pressure was performed. The reduction factors were calculated from the known activation energies of redistribution of the interstitial-type defects investigated. No significant changes of  $\beta$  as a function of pressure were observed. The pressure dependences of the Ni-C and Fe-Si-C disaccommodations were only determined up to about 4 kbar because of the reduction of the yield strength of Cu-Be alloys above 100 °C, and because the pressure-transmitting fluid became very viscous above

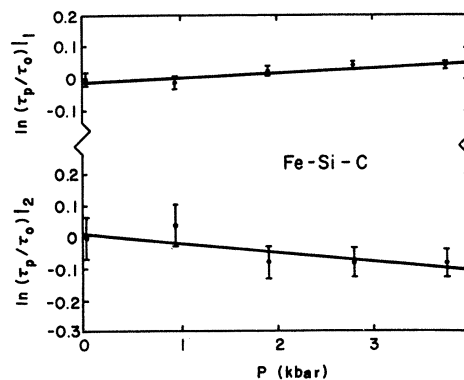


FIG. 3. Pressure dependence of the relaxation time of carbon redistribution in a Fe-1.4 wt% Si - 0.003 wt% C alloy measured at -21 °C.  $\tau_p$  is the relaxation time at pressure  $p$  and  $\tau_0$  the relaxation time at ambient pressure.

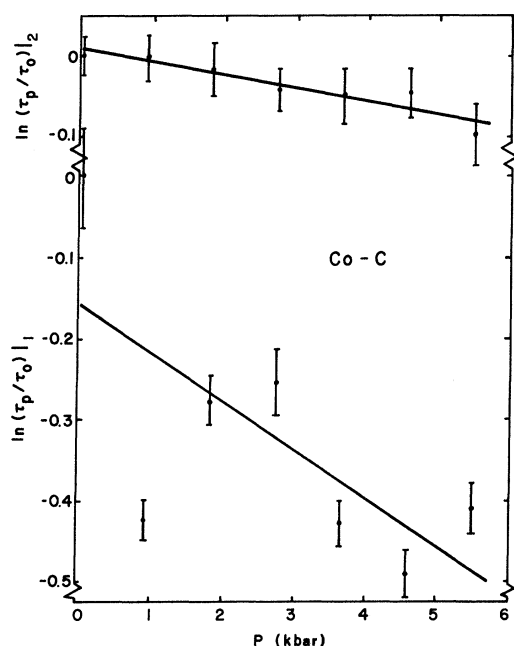


FIG. 4. Pressure dependence of the relaxation time of carbon redistribution in a hcp Co-0.37 wt% C alloy measured at 75 °C.  $\tau_p$  is the relaxation time at pressure  $p$  and  $\tau_0$  the relaxation time at ambient pressure.

4 kbar at -21 °C.

As will be seen below, the activation volume of diffusion is given by

$$\Delta V = \left( \frac{\partial \Delta \phi}{\partial P} \right)_{M,T},$$

where  $\Delta \phi$  is the free activation energy of diffusion. In conjunction with the Arrhenius equation for the relaxation time,

$$\tau = \nu_0^{-1} e^{\Delta \phi / RT}.$$

This yields for the activation volume of diffusion

$$\Delta V = RT \left[ \frac{\partial (\ln \tau)}{\partial P} \right]_{M,T}. \quad (1)$$

The pressure dependence of the attack frequency was neglected as it has been shown that its contribution to  $\Delta V$  is minor.<sup>1</sup> The solid lines in Figs. 2-4 represent least-squares fits of the calculated relaxation times to Eq. (1). The resulting activation volumes of diffusion are collected in Table II in the column  $\Delta V_{\text{expt}}$ . Again, the error limits are the 95% confidence limits as obtained from this analysis. It can be seen that within the error limits, nearly all relaxation times fall on the calculated straight line. The exception is the short-time relaxation time for carbon redistribution in cobalt indicated by the subscript 1 in Fig. 4. Similarly, unsatisfactory results were obtained for this relaxation previously<sup>6</sup> despite considerable efforts to achieve better reproducibility. The reasons for this lack of quality are not known. Table II also contains values of the activation volume of carbon diffusion in Fe determined by different authors. It can be seen that within the

TABLE II. Activation volumes of interstitial diffusion in ferromagnetic metals and alloys.

Metal	Interstitial	$\Delta G$ (kcal/mole)	$T$ (°K)	$\delta_T$ (Ref. 12) ( $10^{-7}$ bar $^{-1}$ )	$\Delta V_s$ (Ref. 4) (cm $^3$ /mole)	$\Delta V_m$ (cm $^3$ /mole)	$\Delta V_{\text{expt}}$ (cm $^3$ /mole)
Fe	C	19.2 (Ref. 13)	250	-8.5	1.3	-0.7	0.037 $\pm$ 0.033 (Ref. 2)
			250				0.0 $\pm$ 0.1 (Ref. 3)
			1000				11.3 (Ref. 14)
	N	18.4 (Ref. 13)	240	-8.5	1.2	-0.6	-0.040 $\pm$ 0.035 (Ref. 2)
Fe-Si	C(1) (Fe-C-Fe)	19.2 (Ref. 13)	252	-8.5 <sup>a</sup>	1.3	-0.7	+0.3 $\pm$ 0.3
	C(2) (Fe-C-Si)	19.6 (Ref. 5)	252	-8.5 <sup>a</sup>	1.3	-0.7	-0.6 $\pm$ 0.9
hcp Co	C(1)	26.7 (Ref. 6)	348	-7.5 <sup>b</sup>	1.7	-0.8	-1.7 $\pm$ 2.0
	C(2)	25.9 (Ref. 6)	348	-7.5 <sup>b</sup>	1.6	-0.8	-0.5 $\pm$ 0.2
Ni	C	32.2 (Ref. 7)	383	-9.8 (Ref. 15)	2.5	-1.4	1.2 $\pm$ 0.1

<sup>a</sup>It is assumed that  $\delta_T$  for the Fe-Si alloy is equal to  $\delta_T$  of iron.

<sup>b</sup> $\sigma_0^{-1} (\partial \sigma_0 / \partial p)_T$  for polycrystalline and  $\kappa$  for fcc cobalt (Ref. 16) were used.

error limits stated, the activation volumes determined in this work are in agreement with those.

#### IV. DISCUSSION

The experimentally obtained activation volumes  $\Delta V_{\text{expt}}$  are activation volumes of defect redistribution and not necessarily equal to the activation volumes of diffusion or long-range migration. In the case of Fe-C<sup>13</sup> and Ni-C<sup>17</sup> alloys, it has been shown that the activation energies of carbon-defect redistribution are equal to the activation energies of diffusion. This is not necessarily the case for the redistribution of carbon interstitials in Fe-Si sites and in hcp Co.<sup>18</sup> In this section we will ignore this possibility and use the term activation volume of diffusion.

An inspection of the activation volumes  $\Delta V_{\text{expt}}$  listed in Table II shows that some of them are distinctly negative. This result is in disagreement with the rule  $\Delta V \approx \Omega$  mentioned in Sec. I; furthermore, it can not be reconciled with any model based on considerations of the strain energy alone. The strain-energy models, on the other hand, are fairly successful in calculating activation volumes of diffusion in nonferromagnetic solids.<sup>4</sup> This observation leads to the conclusion that the strain-energy model does not apply to ferromagnetic materials. Therefore, in the following an alternate model will be proposed for this class of solids.

All models that have been made in the past with the goal of calculating diffusion parameters are equilibrium models. While such an approach is conceptually not satisfying,<sup>19,20</sup> the results of the equilibrium models<sup>4,5,21,22</sup> agree reasonably well with experimental observations. This in itself justifies this approach. Therefore, equilibrium thermodynamics will be used in this discussion. In addition, it will be assumed that the defect properties are essentially determined by the macroscopic properties of the host solid.

In ferromagnetic solids it is appropriate to consider the free energy

$$\phi(P, T, M) = VP - ST + HM.$$

The free energy of activation is then given by

$$\phi' - \phi = (V' - V)P - (S' - S)T + (H' - H)M,$$

where the unprimed and primed quantities refer to the equilibrium and activated states, respectively. The equilibrium state is subject to constraints which eliminate one degree of freedom.<sup>23</sup> Traditionally, this equation is written as

$$\Delta\phi = \Delta VP - \Delta ST + \Delta HM.$$

Consequently, the activation volume of diffusion is given by

$$\Delta V = \left( \frac{\partial \Delta\phi}{\partial P} \right)_{T, M}.$$

This expression is equivalent to the empirical relationship between the activation energy and entropy originally proposed by Zener, and which has recently been put on a sounder basis.<sup>24</sup>

An estimate of the activation volume of diffusion must start with the question of the nature of  $\Delta\phi$ . If  $\Delta\phi$  is essentially a strain energy, it may be expressed by

$$\Delta\phi_s = \frac{1}{2} VC(\Delta\epsilon)^2,$$

where  $C$  is a suitable shear modulus and  $\Delta\epsilon$  signifies the deformation of the crystal characteristic of the activated state. If  $\Delta\epsilon$  is independent of pressure, it follows that the activation volume is given by the pressure dependence of the shear modulus. Expressed in terms of the Grüneisen parameter, the result is<sup>4</sup>

$$\Delta V_s = 2(\gamma - \frac{1}{3})\kappa\Delta\phi,$$

where  $\gamma$  is the Grüneisen parameter,  $\kappa$  the compressibility, and  $\Delta\phi$  the free activation energy of diffusion. The values of  $\Delta V_s$  of the alloys investigated in this study are listed in Table II. More sophisticated strain-energy models<sup>25</sup> yield similar values for close-packed structures, but smaller values for more open structures such as the bcc structure.

As mentioned above, for ferromagnetic solids the assumption  $\Delta\phi \approx \Delta\phi_s$  is questionable; rather  $\Delta\phi$  should be given by the sum of the strain and magnetic energies. The latter is, in turn, the sum of the magnetoelastic, the anisotropy, and the exchange energies. Hence,

$$\Delta\phi_m = \Delta\phi_s + \Delta\phi_{\text{me1}} + \Delta\phi_{\text{an}} + \Delta\phi_{\text{ex}}.$$

The three magnetic terms will contribute to  $\Delta V_m$  in proportion to their pressure derivatives and their absolute values. The contribution of the anisotropy energy can thus be neglected because  $\Delta\phi_{\text{an}} \ll \Delta\phi_{\text{ex}}$ , and since the pressure derivatives of the anisotropy and exchange energies are of comparable magnitude.<sup>12</sup> Therefore, the activation volume of diffusion of a ferromagnetic solid is given by

$$\Delta V_m = \left( \frac{\partial \Delta\phi_s}{\partial P} \right)_{M, T} + \left( \frac{\partial \Delta\phi_{\text{me1}}}{\partial P} \right)_{M, T} + \left( \frac{\partial \Delta\phi_{\text{ex}}}{\partial P} \right)_{M, T}.$$

The leading terms of the series expansions of  $\Delta\phi_s$  and  $\Delta\phi_{\text{me1}}$  are quadratic and linear in the deformation parameters, respectively. The variation of  $\Delta\phi_{\text{ex}}$  with the deformation parameters is not precisely known. It is known, however, that the ferromagnetic-exchange interaction depends very sensitively on the interionic distance, i.e., the leading term in the series expansion of  $\Delta\phi_{\text{ex}}$  depends stronger than quadratically on the deformation parameters. Therefore, to a first approximation the first two terms in the above equation may

be neglected yielding

$$\Delta V_m = \left( \frac{\partial \Delta \phi_{ex}}{\partial P} \right)_{M,T}.$$

Since,  $\Delta \phi_{ex} = VH\Delta M$ , it follows that

$$\Delta V_m = \left[ -\kappa + (\Delta H)^{-1} \left( \frac{\partial \Delta H}{\partial P} \right)_{M,T} \right] VH\Delta M.$$

The quantity  $\Delta M$  is the difference of the saturation magnetization of the crystal in the activated and equilibrium states, respectively. It is, like  $\Delta \epsilon$  in the strain-energy model, a quantity characteristic of the activation process and may be treated as a constant at temperatures sufficiently below the Curie temperature. The energy  $VH\Delta M$  comprises a certain fraction of the free activation energy  $\Delta \phi$ ,

$$VH\Delta M = \delta_1 \Delta \phi, \quad 0 \leq \delta_1 \leq 1.$$

Taking into account that

$$H^{-1} \left( \frac{\partial H}{\partial P} \right)_{M,T} = -H^{-1} \left( \frac{\partial H}{\partial M} \right)_{P,T} \left( \frac{\partial M}{\partial P} \right)_{H,T}, \quad M = \chi H$$

and

$$\sigma_0^{-1} \left( \frac{\partial \sigma_0}{\partial P} \right)_H = M_0^{-1} \left( \frac{\partial M_0}{\partial P} \right)_H - \kappa,$$

where  $\sigma_0$  is the saturation magnetization per unit mass, the activation volume of diffusion of a ferromagnetic solid is given by

$$\Delta V_m = - \left[ \sigma_0^{-1} \left( \frac{\partial \sigma_0}{\partial P} \right)_{H,T} + 2\kappa \right] \delta_1 \Delta \phi.$$

Upper limits ( $\delta_1 = 1$ ) of  $\Delta V_m$  for the alloys of interest are listed in Table II in which the abbreviation

$$\delta_T = - \left[ \sigma_0^{-1} \left( \frac{\partial \sigma_0}{\partial P} \right)_H + 2\kappa \right]_T$$

is used. In calculating  $\delta_T$ , room-temperature values of the pressure dependence of the saturation magnetization and the compressibility were used. Hence, the fact that the disaccommodation runs were made at temperatures different from room

temperature was neglected. This approach is justified as the temperature corrections would be small and therefore need not be considered in this approximation.

None of the experimentally determined activation volumes  $\Delta V_{\text{expt}}$  is equal to either of the limiting values  $\Delta V_s$  or  $\Delta V_m$ , listed in Table II. In view of the many approximations made, close agreement of  $\Delta V_{\text{expt}}$  with either  $\Delta V_s$  or  $\Delta V_m$  cannot be expected. However, it can be seen from Table II that

$$\Delta V_m \leq \Delta V_{\text{expt}} \leq \Delta V_s$$

in all cases but one.<sup>26</sup> This might reflect the fact that in ferromagnetic solids the activation volume is composed of two terms:

$$\Delta V_{\text{expt}} = (1 - \delta) \Delta V_s + \delta \Delta V_m.$$

The constant  $\delta$  indicates to what extent the "ferromagnetic anharmonicity" controls the activation process. Values of  $\delta$  for the three ferromagnetic metals may be calculated from Table II. The results of this calculation in which only the most reliable values of  $\Delta V_{\text{expt}}$  were used for each metal are

$$\delta_{Fe} \approx 0.7, \quad \delta_{Co} \approx 0.9, \quad \delta_{Ni} \approx 0.3.$$

The present approach represents in effect a ferromagnetic Grüneisen continuum model. Therefore, the absolute magnitudes of  $\delta$  should not be taken too seriously. It is interesting to note, though, that  $\delta$  is roughly proportional to the saturation magnetization as it should be. All values of  $\delta$  are much larger than would be expected from a comparison of the magnitudes of the exchange and activation energies. This confirms qualitatively the assumption of the controlling influence of the "ferromagnetic anharmonicity" on the activation process made in the beginning of this discussion.

#### ACKNOWLEDGMENTS

The authors wish to thank Professor T. Suzuki and Dr. H. Sekizawa for valuable discussions. Professor A. Ruoff furnished some calibrated manganin wire for the early stages of the work.

\*Work supported by the American Iron and Steel Institute. It also benefitted from support by the National Science Foundation.

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<sup>26</sup>Concerning the value of  $11.3 \text{ cm}^3 \text{ mole}^{-1}$  (Ref. 14), it is noted that the value of  $\delta_T$  of ferromagnetic solids close to the Curie temperature is often quite large and negative [H. Ebert and A. Kussman, *Z. Physik* **38**, 437 (1937)]. If this is the case for iron, a value of  $11.3 \text{ cm}^3 \text{ mole}^{-1}$  might not disagree with the magnetic energy model.

PHYSICAL REVIEW B

VOLUME 3, NUMBER 3

1 FEBRUARY 1971

## Magnetic Structure of $\text{RbMnCl}_3$

M. Melamud, J. Makovsky, and H. Shaked

*Nuclear Research Centre - Negev, P.O.B. 9001, Beer-Sheva, Israel*

and

S. Shtrikman

*Weizmann Institute of Science, Department of Electronics, Rehovot, Israel*

(Received 24 July 1970)

The compound  $\text{RbMnCl}_3$  is paramagnetic at room temperature and belongs to the space group  $D_{6h}^4-P6_3/mmc$  with six molecules per unit cell. Neutron diffraction of  $\text{RbMnCl}_3$ -powder sample was studied as a function of the sample temperature. A transition to antiferromagnetism was found at  $T_N \sim 94^\circ\text{K}$ . The magnetic structure determined from the diffraction pattern at  $4.2^\circ\text{K}$  consists of ferromagnetic planes stacked in the sequence  $A(+)$ ,  $B(-)$ ,  $B(+)$ ,  $A(-)$ ,  $C(+)$ ,  $C(-)$ , along the  $c$  axis. Spin direction is perpendicular to the  $c$  axis, defining an infinite number of structures which belong to a two-dimensional irreducible representation  $\Gamma_6^*$  of  $D_{6h}^4$ . Two distinctly different structures of orthorhombic symmetry,  $Cm'c'm$  and  $Cmcm$ , span the subspace of this representation and are consistent with the diffraction data. Dipolar energy calculations show that the direction perpendicular to the  $\hat{z}$  direction is of lower dipolar energy than that parallel to  $\hat{z}$ . The existence of a spin component perpendicular to  $\hat{z}$  is also confirmed with the aid of an external magnetic field. A magnetic moment of  $4.1 \mu_B$  is calculated for the  $\text{Mn}^{2+}$  ion from the diffraction pattern at  $4.2^\circ\text{K}$ .

### INTRODUCTION

The compound  $\text{RbMnCl}_3$  was previously investigated by means of x rays,<sup>1-3</sup> and by paramagnetic and antiferromagnetic resonance.<sup>4,5</sup> It was reported<sup>1,2</sup> to be of the hexagonal  $\text{BaTiO}_3$  type, which belongs to the space group  $D_{6h}^4-P6_3/mmc$ , with six formula units per unit cell. ( $a_0 = 7.164$ ,  $c_0 = 17.798$ ,  $c_0/a_0 = 2.484$ <sup>1</sup>;  $a_0 = 7.165$ ,  $c_0 = 17.815$ ,  $c_0/a_0 = 2.486$ <sup>2</sup>. These values are in agreement within their error limits.) The six magnetic ions in this structure occupy the  $2a$  and  $4f$  sites (Fig. 1). According to Tiskhchenko,<sup>3</sup>  $\text{RbMnCl}_3$  belongs to the same space group, but has only two formula units per unit cell, and therefore is of the  $\text{CsNiCl}_3$  type. We shall see below that our data are consistent with the  $\text{BaTiO}_3$ -type structure and are inconsistent with the

$\text{CsNiCl}_3$ -type structure.  $\text{RbMnCl}_3$  was reported to be antiferromagnetic<sup>1</sup> with the spins of the  $\text{Mn}^{2+}$  ions

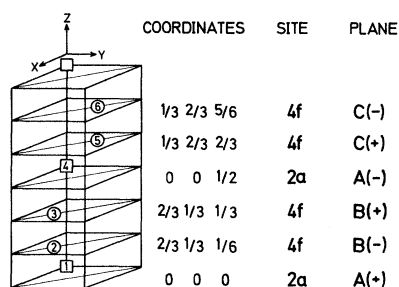


FIG. 1. Positions of  $\text{Mn}^{2+}$  ions in the unit cell. A, B, C denote the threefold axes on which the ions are placed.