

## Diffusion of Zinc and Iron in Pure Cobalt and Diffusion of Iron in Two Iron-Cobalt Alloys\*

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Recebido em 13 de Maio de 1973

The diffusion coefficients  $D$  of radioactive  $Fe^{59}$  and  $Zn^{65}$  in single crystals of pure Cobalt and  $Fe^{59}$  in single crystals of Co-6%-Fe and Co-10%-Fe are measured using Gruzin's residual activity method over the range 808°C–1300°C. Pure cobalt and the alloys undergo a ferromagnetic-paramagnetic transition in this temperature range. A plot  $\ln D$  vs.  $(1/T)$ , where  $D$  is the diffusivity and  $T$  is absolute temperature, deviates from linearity in the neighborhood of the Curie temperature.

Os coeficientes de difusão dos elementos radioativos  $Fe^{59}$  e  $Zn^{65}$  em cristais únicos de cobalto puro e de  $Fe^{59}$  em cristais únicos das ligas Co-6%-Fe e Co-10%-Fe foram medidos, usando-se o método da atividade residual de Gruzin, no intervalo de temperatura 808°C–1300°C. O cobalto puro e as ligas acima mencionadas experimentam uma mudança de fase ferromagnética-paramagnética neste intervalo de temperatura. Um gráfico  $D$  vs.  $1/T$  onde  $D$  é o coeficiente de difusão e  $T$  é a temperatura absoluta, desvia-se da linearidade na vizinhança da temperatura de Curie de cada um dos materiais estudados.

### Introduction

The influence of ferromagnetic transitions upon diffusion in metals and alloys has been reported by several authors<sup>1-8</sup>. It is observed, at the onset of ferromagnetism, that the relation between the diffusion coefficient and temperature deviates from the customarily expected Arrhenius relationship. The diffusion coefficient  $D$  below the Curie point is significantly lower than the expected from an extrapolation of the high temperature data. This decrease in the diffusivity is accompanied with an increase in the activation energy in the ferromagnetic phase.

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\*This research was supported by the *Conselho Nacional de Pesquisas*, Brasil.

For diffusion via a vacancy mechanism.  $D$  is given by<sup>9</sup>

$$D = f a^2 v \exp\left(-\frac{\Delta G_v + \Delta G_m}{RT}\right) = f a^2 v \exp\left(\frac{\Delta S_m + \Delta S_v}{R}\right) \times \quad (1)$$

$$\times \exp\left(\frac{-\Delta H_v + \Delta H_m}{RT}\right), \quad (1)$$

where  $f$  = correlation factor.  $v$  = vibrational frequency in the direction of unit jump (usually considered to be equal to the Debye frequency),  $a$  = lattice parameter. the subscripts  $m$  and  $v$  refer to the motion and formation of vacancies, and the remaining symbols have their usual thermodynamic meaning in the Lewis<sup>10</sup> thermodynamic system of notation. Measured diffusion coefficients in metals and alloys, over a wide range of temperatures, often fit an Arrhenius equation:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right), \quad (2)$$

where both the activation energy  $Q$  and frequency factor  $D_0$  are independent of temperature. If  $f$ ,  $a$ ,  $v$ ,  $\Delta S = \Delta S_v + \Delta S_m$ , and  $\Delta H = \Delta H_v + \Delta H_m$  are temperature independent, we obtain, by comparing Eqs. (1) and (2),

$$Q = \Delta H = \Delta H_v + \Delta H_m. \quad (3)$$

$$D_0 = f a^2 v \exp\left(\frac{\Delta S}{R}\right) \quad (4)$$

One explanation of the so called " $\Delta Q = Q_{\text{ferro}} - Q_{\text{para}}$  effect" was advanced by the authors<sup>11</sup> studying the diffusion of  $\text{Co}^{60}$  in 100% Co, Co-6% Fe, Co-8% Fe and Co-10% Fe and by measuring the elastic constants in the same alloys.

The aim of the present measurement is to study the behavior of other diffusing elements, namely  $\text{Zn}^{65}$  and  $\text{Fe}^{59}$ , in the same alloys where diffusivity of cobalt was extensively studied.

## Experimental Procedure

Disc specimens about 10 mm in diameter by 2 mm thick were prepared from cylindrical single crystals provided by Alpha *Inorganic*. The diffe-

| T(°C) | ← 100% Co →            |                                 | ← 94% Co →             |                                 | ← 90% Co →             |                                 |
|-------|------------------------|---------------------------------|------------------------|---------------------------------|------------------------|---------------------------------|
|       | t(sec)                 | D(cm <sup>2</sup> :sec)         | t(sec)                 | D(cm <sup>2</sup> sec)          | t(sec)                 | D(cm <sup>2</sup> /sec)         |
| 1300  | 2.35 × 10 <sup>4</sup> | (7.6 ± 1.1) × 10 <sup>-10</sup> | 1.06 × 10              | (4.3 ± 0.6) × 10 <sup>-10</sup> | 6.41 × 10              | (3.0 ± 0.4) × 10 <sup>-10</sup> |
| 1253  | 3.07 × 10 <sup>3</sup> | (4.8 ± 0.7) × 10 <sup>-10</sup> | 5.48 × 10              | (2.4 ± 0.4) × 10 <sup>-10</sup> | 3.31 × 10              | (1.8 ± 0.3) × 10 <sup>-10</sup> |
| 1211  | 1.50 × 10 <sup>4</sup> | (2.5 ± 0.4) × 10 <sup>-10</sup> |                        |                                 | 1.38 × 10              | (9.0 ± 1.3) × 10 <sup>-11</sup> |
| 1178  | 5.30 × 10 <sup>4</sup> | (1.6 ± 0.3) × 10 <sup>-10</sup> | 1.85 × 10 <sup>4</sup> | (9.0 ± 1.3) × 10 <sup>-11</sup> | 1.39 × 10              | (5.6 ± 0.8) × 10 <sup>-11</sup> |
| 1154  | 9.52 × 10 <sup>3</sup> | (9.4 ± 1.4) × 10 <sup>-11</sup> | 6.97 × 10 <sup>3</sup> | (5.2 ± 0.8) × 10 <sup>-11</sup> |                        |                                 |
| 1111  | 8.26 × 10 <sup>3</sup> | (4.8 ± 0.7) × 10 <sup>-11</sup> | 8.85 × 10 <sup>4</sup> | (3.0 ± 0.4) × 10 <sup>-11</sup> | 3.04 × 10 <sup>4</sup> | (1.9 ± 0.3) × 10 <sup>-11</sup> |
| 1070  |                        |                                 | 1.66 × 10 <sup>5</sup> | (1.3 ± 0.2) × 10 <sup>-11</sup> | 1.82 × 10 <sup>5</sup> | (8.6 ± 1.3) × 10 <sup>-12</sup> |
| 1030  |                        |                                 | 3.20 × 10 <sup>4</sup> | (6.4 ± 1.0) × 10 <sup>-12</sup> | 6.57 × 10 <sup>5</sup> | (3.8 ± 0.6) × 10 <sup>-12</sup> |
| 1004  | 1.50 × 10 <sup>4</sup> | (6.0 ± 0.9) × 10 <sup>-12</sup> |                        |                                 |                        |                                 |
| 1001  |                        |                                 | 6.21 × 10 <sup>5</sup> | (3.0 ± 0.4) × 10 <sup>-12</sup> | 6.50 × 10 <sup>5</sup> | (2.0 ± 0.3) × 10 <sup>-12</sup> |
| 950   | 6.57 × 10 <sup>5</sup> | (2.0 ± 0.3) × 10 <sup>-12</sup> | 1.15 × 10 <sup>5</sup> | (1.0 ± 0.2) × 10 <sup>-12</sup> | 2.89 × 10 <sup>5</sup> | (7.2 ± 1.1) × 10 <sup>-13</sup> |
| 904   | 8.40 × 10 <sup>5</sup> | (7.8 ± 1.2) × 10 <sup>-13</sup> |                        |                                 |                        |                                 |
| 900   |                        |                                 | 4.08 × 10 <sup>4</sup> | (3.6 ± 0.5) × 10 <sup>-13</sup> | 6.25 × 10 <sup>5</sup> | (2.5 ± 0.4) × 10 <sup>-13</sup> |
| 852   |                        |                                 | 1.60 × 10 <sup>6</sup> | (1.3 ± 0.2) × 10 <sup>-13</sup> | 1.82 × 10 <sup>6</sup> | (7.2 ± 1.1) × 10 <sup>-14</sup> |
| 850   | 8.19 × 10 <sup>5</sup> | (1.9 ± 0.3) × 10 <sup>-13</sup> |                        |                                 |                        |                                 |
| 808   | 1.40 × 10 <sup>5</sup> | (7.2 ± 1.1) × 10 <sup>-14</sup> |                        |                                 |                        |                                 |

Table I - Diffusion of Fe<sup>59</sup> in Fe-Co alloys

|         | Q <sub>Para</sub> (kcal) | Q <sub>Ferro</sub> (kcal) | D <sub>O Para</sub> (cm <sup>2</sup> /sec) | D <sub>O Ferro</sub> (cm <sup>2</sup> sec) | Q <sub>Ferro</sub> - Q <sub>Para</sub> | D <sub>O Ferro</sub> - D <sub>O Para</sub> |
|---------|--------------------------|---------------------------|--|--|--|--|
| 100% Co | 59.4 ± 1.8               | 62.6 ± 1.8                | .16 ± 0.04                                 | .34 ± 0.09                                 | 3.2 ± 2.6                              | .18 ± 0.10                                 |
| 94% Co  | 61.3 ± 1.8               | 65.3 ± 2.0                | .15 ± 0.04                                 | .58 ± 0.14                                 | 4.0 ± 2.7                              | .43 ± 0.30                                 |
| 90% Co  | 62.9 ± 1.8               | 66.7 ± 2.0                | .18 ± 0.05                                 | .68 ± 0.17                                 | 3.8 ± 2.7                              | .50 ± 0.18                                 |

Table II

rence in the thickness of each disc at various points was less than 0.1% of the average specimen thickness. The plated specimen were prepared as outlined in Ref. 12.  $Zn^{60}$  decays with the emission of 0.326 meV, and 0.511 meV and 1.114 meV gamma rays and has a half-life of 245 days. On other hand,  $Fe^{59}$  decays with the emission of 0.27 and 0.46 beta and 1.098 and 1.298 meV gamma rays and has a half-life of 45 days. A thin layer of isotope, about 0.2 microns thick, was electroplated into the end-face of each specimen. The plated specimens had an activity  $A$ , varying from 6,000 to 10,000 counts per minute and per  $cm^2$ . The activity was monitored with a Multichannel Gamma spectrometer system consisting of a 1024 channel analyzer and a shielded 3 x 3 NaI(Tl) scintillation crystal detector. Both 1.098 and 1.298 meV gamma rays of  $Fe^{59}$  were counted. In the case of  $Zn^{60}$ , only the 1.114 meV gamma rays were counted. The counts in each measurement were corrected for the background. For the plating of  $Zn^{65}$ , the solution was  $AlCl_3$  (20 g/l) and  $Na_2SO_4$  (75 g/l). Radioactive iron ( $Fe^{59}$ ) was plated from a saturate oxalate solution.

The sectioning technique was employed and the diffusivity determined by Gruzin's residual activity method<sup>13</sup>. The specimens were annealed in argon atmosphere. After the diffusion anneal the plated area of the specimen was first abraded in order to remove the initial plated layer of radioactive material, and then the radioactivity  $A_I$  of the specimen was recorded and used as a reference value. Thin layers (1-4 microns thick) were then removed by grinding the specimen parallel to its plated surface on 4/0 grade emery paper, then polished on a rotating wheel. The sample activity was measured after each removal. The penetration is determined by successive weightings of the disc with a semi-microbalance. Curves of activity vs. thickness removed were obtained. The slopes at various points were measured and their logarithms plotted as a function of the square of thickness removed. The slope of  $\ln\left(\frac{\partial A}{\partial x}\right)$  vs.  $x^2$  yields a value of  $(1/4Dt)$

for each fixed temperature. where  $t$  is the annealing time. A plot of  $\ln D$  vs.  $(1/T)$  allows the determination of the activation energy  $Q$  and frequency factor  $D_0$ . Errors in the diffusivity result mainly from the determination of (1) the activity, (2) the thickness of layers removed, and (3) the annealing time. An overall error of about 15% was assigned to the values of  $D$ . The error limits assigned to  $Q$  are obtained by first estimating the maximum and minimum slopes which can be drawn through the data and calculating an energy for each slope. Sixty per cent of the difference between these two values is taken to be the final value of the uncertainty in  $Q$ . On the average, the probable errors are about  $\pm 25\%$  in  $D_0$ .

| $T(^{\circ}\text{C})$ | $t(\text{sec})$    | $D(\text{cm}^2:\text{sec})$     |
|-----------------------|--------------------|---------------------------------|
| 1240                  | $4.80 \times 10^4$ | $(1.2 \pm 0.2) \times 10^{-10}$ |
| 1200                  | $1.70 \times 10^4$ | $(7.4 \pm 1.1) \times 10^{-11}$ |
| 1162                  | $3.0 \times 10^4$  | $(4.0 \pm 0.6) \times 10^{-11}$ |
| 1140                  | $7.14 \times 10^3$ | $(2.5 \pm 0.4) \times 10^{-11}$ |
| 1115                  | $2.41 \times 10^4$ | $(1.5 \pm 0.3) \times 10^{-11}$ |
| 1080                  | $1.72 \times 10^4$ | $(5.2 \pm 0.8) \times 10^{-12}$ |
| 1000                  | $2.07 \times 10^5$ | $(1.3 \pm 0.2) \times 10^{-12}$ |
| 960                   | $1.61 \times 10^5$ | $(5.0 \pm 0.8) \times 10^{-13}$ |
| 900                   | $3.70 \times 10^5$ | $(1.3 \pm 0.2) \times 10^{-13}$ |

**Table III:** Diffusion coefficient of  $\text{Zn}^{65}$  in 100% Co

| $Q_{\text{Para}}(\text{kcal})$ | $Q_{\text{Ferro}}(\text{kcal})$ | $D_{0\text{Para}}$ | $D_{0\text{Ferro}}$ | $Q_{\text{Ferro}} - Q_{\text{Para}}$ | $D_{0\text{Ferro}} - D_{0\text{Para}}$ |
|--------------------------------|---------------------------------|--------------------|---------------------|--------------------------------------|--|
| $60.8 \pm 1.8$                 | $63.7 \pm 1.9$                  | $.08 \pm 0.2$      | $.12 \pm .03$       | $2.9 \pm 2.6$                        | $.04 \pm .04$                          |

**Table IV**

## Results and Discussion

The diffusion coefficients as a function of temperature for  $\text{Fe}^{59}$  in: 100% Co, Co-6% Fe and Co-10% Fe alloys and of  $\text{Zn}^{65}$  in pure cobalt are shown in Figs. 1-4. Except for a temperature range just above and below the Curie temperature, linearity between  $\ln D$  and  $(1/T)$  is observed in both the paramagnetic and the ferromagnetic states. A least squares fit yields the values of  $D$ ,  $Q$  and  $D_0$  listed in Tables I to IV. The diffusion coefficients are given by

$$\text{Co 100\% Ferromagnetic region } D_{\text{Fe}59} = 0.34 \exp\left(-\frac{62,000}{RT}\right),$$

$$D_{\text{Zn}65} = 0.12 \exp\left(-\frac{63,700}{RT}\right),$$

$$\text{Paramagnetic region } D_{\text{Fe}59} = 0.16 \exp\left(-\frac{59,400}{RT}\right),$$

$$D_{\text{Zn}65} = 0.08 \exp\left(-\frac{60,800}{RT}\right):$$

Co-6% Fe Ferromagnetic region  $D_{Fe^{59}} = 9.58 \exp\left(-\frac{65,300}{RT}\right)$ ,

Paramagnetic region  $D_{Fe^{59}} = 9.15 \exp\left(-\frac{66,700}{RT}\right)$

Co-10% Fe Ferromagnetic region  $D_{Fe^{59}} = 0.68 \exp\left(-\frac{66,700}{RT}\right)$ ,

Paramagnetic region  $D_{Fe^{59}} = 0.18 \exp\left(-\frac{62,900}{RT}\right)$ .

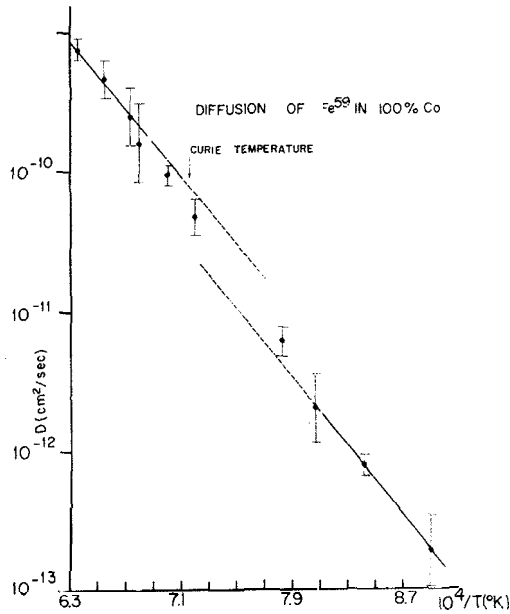


Fig. 1

The present results for the diffusion of  $Fe^{59}$  in 100% Co compare well, within the experimental errors, with those reported by Badia and Vignes<sup>14</sup>. No results, to the best of our knowledge, have been reported on the diffusion of  $Zn^{65}$  in 100% Co, and on the diffusion of  $Fe^{59}$  in the alloys studied in the present experiment. Note from Tables II and IV that the para-ferromagnetic transitions leads to an increase both in the activation energy

( $\Delta Q = Q_{\text{ferro}} - Q_{\text{para}}$ ) and frequency factor ( $D_{0\text{ferro}} - D_{0\text{para}}$ ) for both diffusing elements. The present results and those relating the diffusion of  $\text{Co}^{60}$  in a 100% Co, reported in Ref. 11, namely,  $AQ = 3.1$  kcal/mole, allow us to investigate, from an experimental point of view, the dependence of  $AQ$  on the spin state of the diffusing element. Atomic zinc, cobalt and iron have spin magnetic moments of 0, 1.7 and 2.2 Bohr magnetons, respectively. By considering the matrix of pure cobalt, one would expect, if there is any interaction between the spin of host lattice and that of the diffusing element  $AQ$  to increase in the same order. The values for  $AQ$  for the diffusion of zinc, cobalt and iron are 2.9, 3.1 and 3.2 kcal/mole, respectively. The near constancy of these values suggests that the magnetic effect is primarily a property of the host lattice and does not, in the first approximation, depend strongly upon the nature of the diffusing specie. A similar conclusion was reached by Lai and Borg<sup>15</sup> by studying the diffusion of gold, nickel and cobalt in alpha iron. The change in  $Q$  with alloying results from a change in the lattice parameter and in the interatomic interactions. In the ferromagnetic phase the exchange interaction between 3d electrons also changes with alloying since the magnetic moment of Fe is larger than that of Co one may expect  $Q_{\text{ferro}}$ , in dilute Co-Fe alloys, to exhibit a larger increase with % Fe than does  $Q_{\text{para}}$ . This is in agreement with the present measurements. The opposite would be true in Co-Ni alloys since the

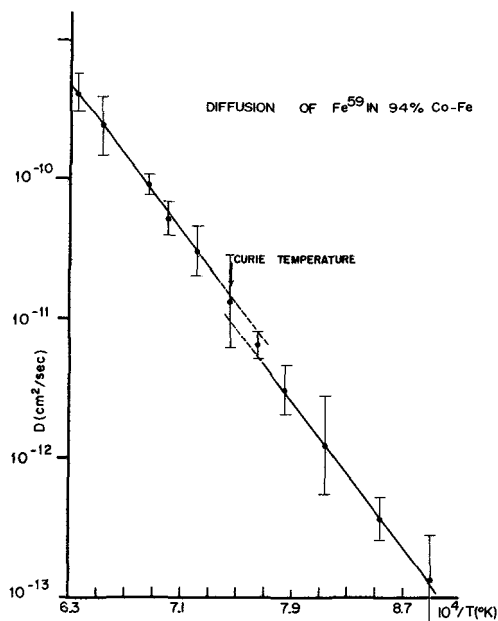


Fig. 2

magnetic moment of Ni is less than that of Co. This is in agreement with the measurements of Hirano *et al.*<sup>8</sup>.

Another aspect of the " $\Delta Q$  effect" that is worthwhile to mention is its dependence on the ionic radius of the diffusing element. The ionic radii of the three elements under discussion are  $\text{Co}^{+2}$  (0.74 Å),  $\text{Fe}^{+2}$  (0.76 Å) and  $\text{Zn}^{+2}$  (0.72 Å). Therefore, the valence and size effects described in Ref. 16 are not strongly operative in this case. The activation energies for the diffusion of each of the three elements in pure cobalt is thus expected to be in close value. This is found to be true in the present experiment for both the paramagnetic and the ferromagnetic region.

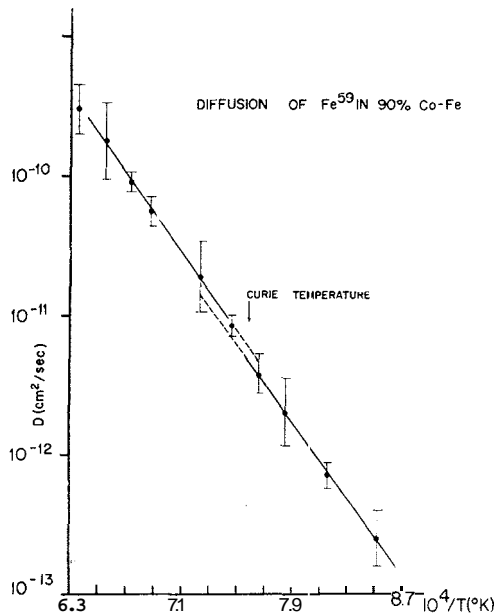
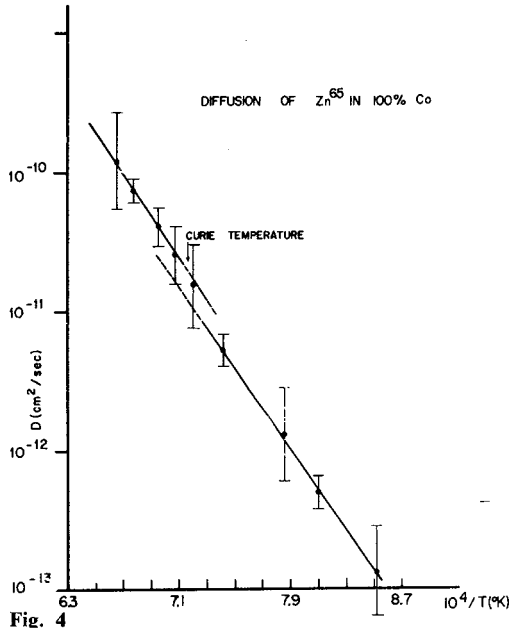


Fig. 3

The above conclusions and the fact that the values of AQ for  $\text{Fe}^9$  in Co-6% Fe and Co-10% Fe are very similar to those found for the diffusion of  $\text{Co}^{60}$  in the same alloys<sup>11</sup>, namely 3.7 kcal/mole and 4.7 kcal/mole for AQ and 0.15  $\text{cm}^2/\text{sec}$  and 0.11  $\text{cm}^2/\text{sec}$  for  $\Delta D_0$  respectively, allow us to apply to the present results, the semi-empirical equation described by the authors in Ref. 11. The statement of that equation was the result of measurements of diffusion of  $\text{Co}^{60}$  in: 100% Co, Co-6% Fe, Co-8% Fe and Co-10% Fe, and the measurements of the elastic constant  $C_{11}$ , as a function of the temperature in the Co-Fe alloys<sup>17</sup>.





Finally, Tables II and IV show that an increase in  $D_0$  in the ferromagnetic phase is also apparent. There is no general agreement from other experimentalists about this observation. Ray and Sharman<sup>7</sup>, Stanley and Wert<sup>6</sup>, and Hirano *et al.*<sup>8</sup> have reported increase in  $D_0$  in the ferromagnetic phase. A single value in both phases has been reported by Borg and Birchnall<sup>3</sup>. However, considering the experimental error in  $D_0$ , conclusions about the magnetic effects upon  $D_0$  do not appear to be warranted at the present time.

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