

Zeitschrift: Helvetica Physica Acta
Band: 41 (1968)
Heft: 6-7

Artikel: Thermoelectric power of magnesium and magnesium alloys
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DOI: <https://doi.org/10.5169/seals-113914>

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Thermoelectric Power of Magnesium and Magnesium Alloys¹⁾

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(18. IV. 68)

Abstract. We report here measurements of the thermoelectric power of commercially pure, polycrystalline magnesium between 5°K and 300°K. The thermopower exhibits a well-defined phonon-drag peak near 60°K. Between 150°K and 300°K, the thermopower follows the relation $S = \alpha T + \delta/T$, where $\alpha = -2.3 \times 10^{-3} \mu\text{V}/(^{\circ}\text{K})^2$ and $\delta = -230 \mu\text{V}$. Thus, in contrast to the monovalent metals, the phonon-drag and diffusion contributions to the total thermopower are of approximately equal magnitude at room temperature. The data on some of the magnesium alloy systems studied by Salkovitz, Schindler and Kammer in 1956, which at that time could not be explained satisfactorily, are reexamined. It is shown that an interpretation which properly accounts for changes of diffusion and phonon-drag due to the addition of solutes is in good agreement with the experimental results.

I. Introduction

Several years ago, SALKOVITZ, SCHINDLER and KAMMER [1, 2] (hereafter referred to as SSK) reported measurements of the thermoelectric power of various magnesium alloys. They analyzed their data, which were limited to room temperature and 78°K, in terms of Friedel's expression [3]

$$\frac{\Delta S}{S_0} = - \left(1 - \frac{\Delta x}{x}\right) \left(1 + \frac{\varrho_0}{\Delta \varrho}\right)^{-1}. \quad (1)$$

Here S_0 is the absolute thermoelectric power of pure magnesium, ΔS is the change in thermopower upon alloying, ϱ_0 is the resistivity of the pure metal and $\Delta \varrho$ the residual resistivity of the alloy; the parameters x and Δx are given by

$$x = - E_F \left(\frac{\partial \ln \varrho_0}{\partial E} \right)_{E_F} \quad (2)$$

$$\Delta x = - E_F \left(\frac{\partial \ln \Delta \varrho}{\partial E} \right)_{E_F} \quad (3)$$

where E_F is the Fermi energy relative to the conduction band edge.

Since the parameter Δx depends on the logarithmic derivative of the residual resistivity, it should be independent of solute concentration c , at least for concentrations sufficiently low that $\Delta \varrho$ is proportional to c . Moreover, since electron-impurity scattering, the process which gives rise to $\Delta \varrho$ is independent of temperature, Δx should be independent of temperature as well.

The experimental results showed, however, that at room temperature Δx did depend upon c , especially at low concentrations; moreover, the changes in ΔS at the

¹⁾ Supported in part by a grant from the National Science Foundation.

lower temperature were much too large to be explained by Equation (1) with the same value of Δx .

The work of SSK was performed at a time when the important role of phonon non-equilibrium, leading to phonon-drag [4], was not yet fully appreciated. These workers, therefore, assumed that the total thermopower of the pure metal, as well as of the alloys, could be attributed entirely to what is now called the 'diffusion' thermopower, and denoted by S_d . In fact, however, as we shall demonstrate presently, even at room temperature S_T^0 , the total thermopower of pure magnesium is due, in about equal measure, to S_g^0 and S_d^0 , the phonon-drag and diffusion contributions, respectively. This result is somewhat unusual since in most cases studied previously, S_g is negligibly small already at 300°K; the only other exception known to us is aluminum [5] whose thermoelectric power bears a close resemblance to that of magnesium.

The difficulty encountered by SSK in their attempt to find a satisfactory interpretation of their results can be traced directly to the neglect of phonon-drag. The crucial point here is that Friedel's expression relates only to the effect of alloying on the diffusion term and sheds no light on the manner in which solutes influence S_g . The work of BLATT and KROPSCHOT [6] and others [7] demonstrated that S_g is generally reduced by alloying primarily as a result of scattering of phonons by imperfections. Thus, for example, impurities such as Ag and Pb, whose masses differ greatly from that of Mg can scatter phonons by virtue of this large mass defect, reduce the phonon mean free path, and effectively quench phonon-drag. A similar situation can arise when the mass difference between solvent and solute atoms is small if the force constants are significantly modified. As a result, additions of impurities to a metal in concentrations of one atomic percent or more frequently reduce S_g^A , the phonon-drag effect in the alloy, to negligible proportions. Evidently, before a sensible analysis of alloy data can be carried out, the relative contributions of S_g^0 and S_d^0 to S_T^0 must first be established.

This we have done by measuring the absolute thermoelectric power of pure magnesium between 5°K and room temperature. The technique employed in these measurements has already been described elsewhere [8] and will not be discussed here.

II. Thermoelectric Power of Pure Magnesium

Our results are shown in Figure 1. The prominent phonon-drag contribution, which reaches its peak near 60°K is quite evident, and it is now apparent why alloy data, especially at 78°K, defied analysis which neglected phonon-drag.

We write the absolute thermopower of magnesium as

$$S_T^0 = S_d^0 + S_g^0. \quad (4)$$

The diffusion term, S_d^0 is expected to depend linearly on temperature. It can be shown [9] that at low temperatures S_g^0 should go as T^3 , whereas at high temperatures S_g^0 should be proportional to $1/T$. Hence we expect

$$S_T^0 = \alpha' T + \beta T^3 \quad \text{low temperatures} \quad (5a)$$

$$S_T^0 = \alpha T + \delta/T \quad \text{high temperatures} \quad (5b)$$

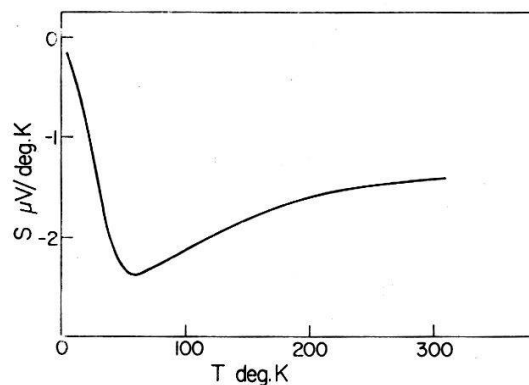


Figure 1

The absolute thermoelectric power of pure magnesium, polycrystalline wire. These results are in excellent agreement with measurements on single crystals by V. ROWE and P. A. SCHROEDER (to be published).

Equation (5a) has been verified for a number of pure metals [10]. The high temperature relation, Equation (5b), is usually not obeyed and experimentally one often finds that S_g^0 decreases more rapidly with temperature than Equation (5b) predicts [11]. The notable, previously known exception to this pattern is aluminum for which S_g^0 does diminish as $1/T$ over a very wide temperature range extending from 300°K to 700°K [5]. We have analyzed our results in terms of Equations (5), plotting S_T^0/T versus T^2 at low temperatures and TS_T^0 versus T^2 at high temperatures. The results are shown in Figures 2 and 3. Evidently, as in aluminum, so also in magnesium the theoretical expectations appear to be fulfilled by observation.

From Figure 2 we obtain

$$\alpha' = -0.04 \mu\text{v}/(^{\circ}\text{K})^2, \quad \beta = -1.2 \times 10^{-5} \mu\text{v}/(^{\circ}\text{K})^4$$

and from Figure 3 we find

$$\alpha = -2.3 \times 10^{-3} \mu\text{v}/(^{\circ}\text{K})^2, \quad \delta = -230 \mu\text{v}.$$

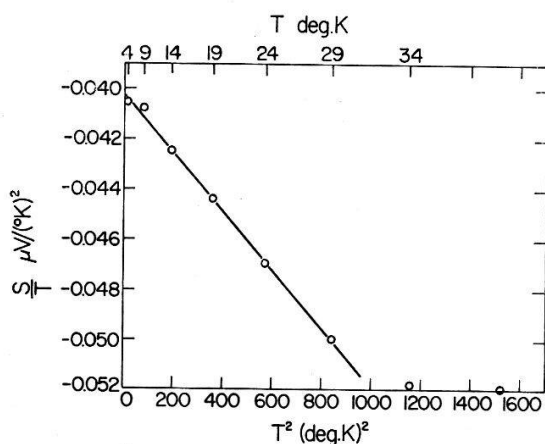


Figure 2

Separation of the thermoelectric power of pure magnesium into diffusion and phonon-drag contribution at low temperatures. $S/T = (-0.04 - 1.2 \times 10^{-5} T^2) \mu\text{v}/(^{\circ}\text{K})^2$.

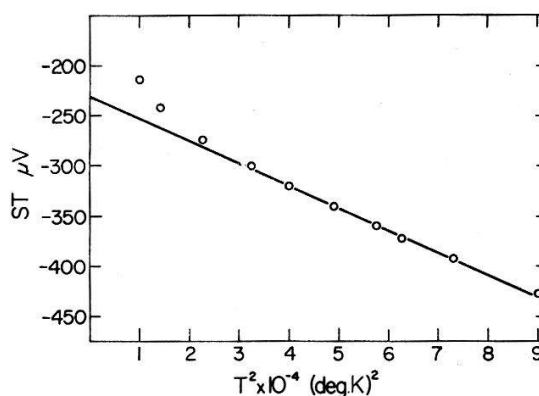


Figure 3

Separation of the thermoelectric power of pure magnesium into diffusion and phonon-drag contributions at high temperature. $TS = (-2.3 \times 10^{-3} T^2 - 230) \mu\text{v}$.

There is a notable discrepancy between the values of α and α' which characterize the diffusion thermopower at high and low temperatures. These two constants should be approximately equal, with α' being perhaps a third as large as α . Instead α' is an order of magnitude greater than α . We are inclined to believe that the high temperature value, i.e. $\alpha = -2.3 \times 10^{-3} \mu\text{V}/(^{\circ}\text{K})^2$, corresponds to the true diffusion thermopower of pure magnesium, and that the unusually large value of α' is due to very small concentrations of magnetic impurities which are known to give rise to Kondo anomalies in this metal [12]. The magnesium wire, which we obtained from the Dow Chemical Co., Midland, Michigan, was nominally 99.99% pure and had a resistance ratio of 275. Although it is, thus, quite 'pure enough' to give reliable values for S_d^0 at room temperature, it is not of sufficient purity to rule out the appearance of thermopower anomalies [13] generally associated with the Kondo effect. In our analysis of the alloy data of SSK we therefore assume that S_d^0 at 78°K is characterized by α rather than α' .

III. Magnesium Alloys

As was mentioned in the introduction, the data of SSK defied analysis in terms of the Friedel relation. The most notable discrepancies appeared in the case of alloys containing aluminum, indium, tin and lead, although also in the case of silver, lithium and cadmium results at 300°K and 78°K could not be reconciled satisfactorily. The former group of alloys exhibited a change in the sign of ΔS , from negative to positive, as the temperature was reduced, suggesting that $\Delta\chi$, and thus the logarithmic derivative $\partial \ln \Delta\rho/\partial E$ must also change sign. If this were true, it would, of course, drastically violate the basic assumptions leading to Equation (1) and could only be explained by the radical assumption that the band structure of the alloy suffers a substantial modification with temperature.

The results of SSK can now, however, be understood very easily. Briefly, the situation is as follows: At room temperature S_g^0 is relatively small, roughly equal to S_d^0 . The total change in thermopower is the sum of ΔS_g and ΔS_d . In the first group of alloys $|S_d|$ is increased and $|S_g|$ decreased by the solutes, the net result being an overall increase of $|S|$, so that $|S_T^A| > |S_T^0|$, i.e. $S_T^A < S_T^0$, at room temperature. At the lower temperature, however, S_g^0 is much larger in magnitude so that the same fractional reduction of $|S_g|$ will now lead to a much larger change in $|S_T|$ toward positive values. At the same time the effect of the solutes on S_d is diminished since $|S_d^0|$ is smaller the lower the temperature. Hence at 78°K the positive change due to the reduction of $|S_g|$ now exceeds the change in $|S_d|$ and $|S_T^A| < |S_T^0|$, i.e. $S_T^A > S_T^0$. Thus in magnesium alloys a change in the sign of ΔS would be expected at some temperature whenever the effect of alloying on the diffusion thermopower is such as to increase its magnitude.

Conforming with the approach generally adopted in recent years we shall use the Gorter-Nordheim (GN) relation [7] rather than Friedel's to analyze some of the data of SSK. The GN relation, which also concerns itself with the diffusion contribution only, may be written

$$S_d^A - S_d^0 \equiv \Delta S_d = \frac{\Delta\rho}{e_A} (S_d^j - S_d^0) \quad (6)$$

where S_d^A and S_d^0 are the diffusion thermopower of the alloy containing solutes of type j and of the pure metal, respectively, and S_d^j is the so-called intrinsic thermopower of solute j in the host lattice. S_d^j should be independent of concentration and a linear function of temperature. Equation (6) is completely equivalent to (1) and rests on the same basic assumptions. In fact, S_d^j and Δx are simply related by

$$S_d^j = \frac{\pi^2 k^2 T}{3 e E_F} \Delta x.$$

Current preference for the GN relation is based principally on convenience in presenting data for a series of binary alloys and the fact that the range of validity of Equation (6) can be deduced from experimental results with relative ease [14].

To apply the GN relation – as Friedel's – one must know not only the thermopowers of the pure substance and of the alloy, but their resistivities as well. Unfortunately, SSK give resistivity results at 300°K only and application of Equation (6) at 78°K must, therefore, rest on somewhat uncertain grounds. We proceed by assuming that the resistivity of their pure magnesium at 78°K is the same as given elsewhere in the literature [15] and make the further assumption that Matthiessen's rule is valid. This last assumption is, however, not justified and represents a rather doubtful approximation. In their paper SSK present evidence for substantial deviations from Matthiessen's rule near 300°K; the deviations are likely to be even more pronounced near 78°K [16]. Although the GN relation may retain its validity even though Matthiessen's rule is violated, it is essential that $\rho_A(T)$ be known to apply Equation (6).

We have selected three alloy systems from the eight studied by SSK. Two of the three display the change in sign of ΔS between 300°K and 78°K which appeared so puzzling and of these one, MgAl, exhibited yet another unexplained feature, a change of sign of ΔS with concentration. The third, MgAg, was included to demonstrate that the arguments apply also to those alloys which show no sign reversal of ΔS . The three alloy systems are among those whose deviations from Matthiessen's rule, at least near 300°K, are relatively small. Nevertheless, it must be emphasized again that our results are, at best, only semiquantitative and merely demonstrate that proper consideration of phonon-drag does resolve an otherwise perplexing difficulty.

We proceed as follows. From the data at 300°K we extract for each alloy system the quantity $(S_d^j - S_d^0)$ and an estimate of the fractional reduction of S_g due to the presence of solutes in concentration c . We then calculate the expected change in the diffusion and phonon-drag contributions to the thermoelectric power at 78°K, subject to the approximations stated above, and assuming, moreover, that the fractional change in S_g is the same at 300°K and 78°K. The calculated and observed changes in thermopower at 78°K are then compared.

The total change in thermopower due to alloying is

$$\Delta S_T = \frac{\Delta \rho}{\rho_A} (S_d^j - S_d^0) + S_g^A - S_g^0$$

where S_g^A is the phonon-drag contribution in the alloy. For dilute alloys $|S_g^A|$, though smaller than $|S_g^0|$, cannot be neglected. We assume a simple relation

$$S_g^A = S_g^0 / (1 + a c)$$

where c is the solute concentration and a is a constant for each alloy system. We find that, with reasonable values of a , a plot of $\Delta S_d = \Delta S_T + S_g^0 - S_g^A$ versus $\Delta \rho / \rho_A$ at 300°K is indeed a straight line whose slope determines $S_d^j - S_d^0$ at that temperature (see Figure 4). According to the GN relation $(S_d^j - S_d^0)$ at 78°K should be given by

$$(S_d^j - S_d^0)_{78} = \frac{78}{300} (S_d^j - S_d^0)_{300}$$

and calculate $(\Delta S_d)_{78}$ from

$$(\Delta S_d)_{78} = \frac{\Delta \rho}{(\rho_A)_{78}} \left(\frac{78}{300} \right) (S_d^j - S_d^0)_{300}.$$

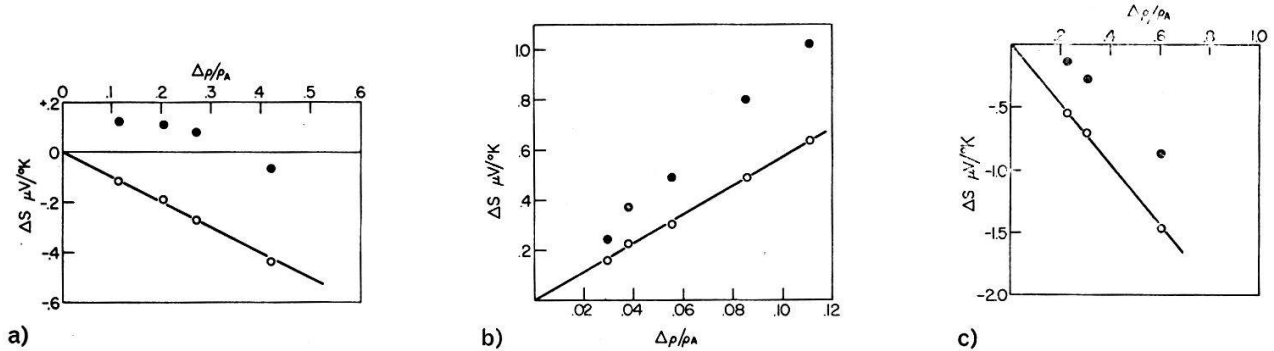


Figure 4

Gorter-Nordheim plots of the change in thermoelectric power at 300°K for (a) MgAl, (b) MgAg and (c) MgPb alloys. The solid points show the total measured change in thermopower. The open circles give the estimated change in diffusion thermopower. The difference between these points corresponds to the change in the phonon-drag thermopower due to alloying.

We estimate $(S_g^A)_{78}$ from

$$(S_g^A)_{78} \approx (S_g^0)_{78} / (1 + a c)$$

where $(S_g^0)_{78}$ is the difference $(S_T^0 - S_d^0)_{78}$ obtained from Figure 1, with $S_d^0 = \alpha T$. The calculated value of ΔS_T is then

$$\begin{aligned} (\Delta S_T)_{calc} &= (\Delta S_d)_{78} + (S_g^A)_{78} - S_T^0 - S_d^0 = (\Delta S_d)_{78} - (S_g^0)_{78} \left(\frac{a c}{1 + a c} \right) \\ &= (\Delta S_d)_{78} + (\Delta S_g)_{78}. \end{aligned}$$

The values of $(\Delta S_T)_{calc}$ and of $(\Delta S_T)_{meas}$ are shown in the Table. Considering the various uncertainties and approximations which we were forced to make, the agreement between these two columns is satisfactory.

IV. Conclusion

Measurements of the absolute thermoelectric power of pure magnesium show that in this metal phonon-drag plays an important role at least to room temperature. The temperature dependence of this phonon-drag contribution appears to conform with elementary theoretical expectations. In particular, it does not diminish with temperature as rapidly as in the monovalent metals.

Table
Thermoelectric power of MgAl, MgAg and MgPb alloys

MgAl: $a_{300} = 1.0/\text{at.}\%$; $(S_d^i - S_d^0)_{300} = -1.0 \mu\text{V}/^\circ\text{K}$; $\varrho_0(78) = 0.55 \mu\Omega\text{-cm}^a$

| c at. % | $\Delta\varrho$ $\mu\Omega\text{-cm}$ | $\varrho_A(78)$ $\mu\Omega\text{-cm}$ | $(\Delta S_d)_{78}$ $\mu\text{V}/^\circ\text{K}$ | $(\Delta S_g)_{78}$ $\mu\text{V}/^\circ\text{K}$ | $(\Delta S_T)_{78}^{calc}$ $\mu\text{V}/^\circ\text{K}$ | $(\Delta S_T)_{78}^{meas}$ $\mu\text{V}/^\circ\text{K}$ | $(\Delta S_T)_{300}^{meas}$ $\mu\text{V}/^\circ\text{K}$ |
|--------------|--|--|---|---|--|--|---|
| 0.29 | 0.582 | 1.132 | -0.134 | +0.405 | +0.271 | +0.28 | +0.121 |
| 0.53 | 1.133 | 1.683 | -0.175 | +0.623 | +0.448 | +0.403 | +0.111 |
| 0.80 | 1.641 | 2.191 | -0.195 | +0.80 | +0.605 | +0.477 | +0.080 |
| 1.64 | 3.238 | 3.788 | -0.222 | +1.12 | +0.898 | +0.692 | -0.032 |

MgAg: $a_{300} = 1.5/\text{at.}\%$; $(S_d^i - S_d^0)_{300} = +5.7 \mu\text{V}/^\circ\text{K}$; $\varrho_0(78) = 0.55 \mu\Omega\text{-cm}^a$

| c at. % | $\Delta\varrho$ $\mu\Omega\text{-cm}$ | $\varrho_A(78)$ $\mu\Omega\text{-cm}$ | $(\Delta S_d)_{78}$ $\mu\text{V}/^\circ\text{K}$ | $(\Delta S_g)_{78}$ $\mu\text{V}/^\circ\text{K}$ | $(\Delta S_T)_{78}^{calc}$ $\mu\text{V}/^\circ\text{K}$ | $(\Delta S_T)_{78}^{meas}$ $\mu\text{V}/^\circ\text{K}$ | $(\Delta S_T)_{300}^{meas}$ $\mu\text{V}/^\circ\text{K}$ |
|--------------|--|--|---|---|--|--|---|
| 0.11 | 0.136 | 0.686 | +0.294 | +0.255 | +0.549 | +0.576 | +0.238 |
| 0.22 | 0.176 | 0.726 | +0.360 | +0.447 | +0.807 | +0.923 | +0.371 |
| 0.33 | 0.261 | 0.811 | +0.476 | +0.596 | +1.072 | +1.232 | +0.491 |
| 0.495 | 0.415 | 0.965 | +0.637 | +0.765 | +1.402 | +1.322 | +0.798 |
| 0.528 | 0.557 | 1.107 | +0.748 | +0.80 | +1.548 | +1.652 | +1.018 |

MgPb: $a = 4.8/\text{at.}\%$; $(S_d^i - S_d^0)_{300} = -2.4 \mu\text{V}/^\circ\text{K}$; $\varrho_0 = 0.55 \mu\Omega\text{-cm}^a$

| c at. % | $\Delta\varrho$ $\mu\Omega\text{-cm}$ | $\varrho_A(78)$ $\mu\Omega\text{-cm}$ | $(\Delta S_d)_{78}$ $\mu\text{V}/^\circ\text{K}$ | $(\Delta S_g)_{78}$ $\mu\text{V}/^\circ\text{K}$ | $(\Delta S_T)_{78}^{calc}$ $\mu\text{V}/^\circ\text{K}$ | $(\Delta S_T)_{78}^{meas}$ $\mu\text{V}/^\circ\text{K}$ | $(\Delta S_T)_{300}^{meas}$ $\mu\text{V}/^\circ\text{K}$ |
|--------------|--|--|---|---|--|--|---|
| 0.24 | 1.332 | 1.882 | -0.444 | +0.962 | +0.518 | +0.478 | -0.143 |
| 0.37 | 2.017 | 2.567 | -0.491 | +1.15 | +0.659 | +0.586 | -0.279 |
| 1.32 | 6.926 | 7.376 | -0.585 | +1.555 | +0.970 | +0.932 | -0.868 |

^a) From G. T. MEADEN, *Electrical Resistance of Metals* (Plenum Press, New York 1965), p. 15.

The results on pure magnesium have been employed in a new analysis of some of the data obtained some years ago by SALKOVITZ, SCHINDLER and KAMMER, which at that time appeared difficult to understand in terms of Friedel's theory. The results demonstrate that alloy data can be understood provided both diffusion and phonon-drag contributions are included in such an analysis.

Acknowledgements

We wish to thank Mr. A. DAVIDSON for assistance in taking the data and the computer analysis thereof, Dr. P. A. SCHROEDER for the loan of the equipment used in the measurements reported here, Dr. A. I. SCHINDLER for stimulating discussions, and the National Science Foundation for financial support of this research project.

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On the Pressure Dependence of the Ferroelectric Properties of KH_2PO_4 and KD_2PO_4

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(25. II. 68)

Abstract. The dependences of the ferroelectric Curie temperatures (T_C), spontaneous polarizations and the Curie-Weiss constants of KH_2PO_4 and KD_2PO_4 on hydrostatic pressure have been evaluated within the protonic order-disorder model, using a four particle cluster approximation. The order of magnitude and sign of the pressure effects as well as the direction of the isotope shifts agree rather well with the recent experimental data of UMEBAYASHI, FRAZER, SHIRANE, DANIELS and SAMARA.

UMEBAYASHI, FRAZER, SHIRANE and DANIELS [1] have recently shown that the ferroelectric Curie temperatures (T_C) of KH_2PO_4 and KD_2PO_4 decrease with increasing hydrostatic pressure and SAMARA [2] found a similar decrease for the Curie-Weiss constant of KD_2PO_4 . These data are in marked contrast with the case of triglycine sulphate [2b] where pressure induces a shift of the Curie point towards higher temperatures. The most interesting result of these studies however, is the discovery