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Deviations from Matthiessen's Rule Due to Phonon Spectrum Changes

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The deviations from Matthiessen's rule which would be expected to result from changes in the phonon spectrum of a metal when chemical or physical defects are introduced, have been analyzed in greater detail within the framework of the Bloch-Grüneisen theory. This work was prompted by certain contradictory statements appearing in the literature, and has led to a clarification of the situation regarding possible changes in the characteristic temperature θ_R. In addition, a fresh assessment of the applicability of this model to more recent experimental results is presented.

INTRODUCTION

The electrical resistivity of metals containing dilute concentrations of chemical or physical defects is to a first approximation given by Mattheissen's rule[1] (MR), which is usually expressed in the form

$$\rho(T)=\rho_i^p(T)+\rho(0) \ , \qquad (1)$$

where $\rho(T)$ and $\rho(0)$ are the measured resistivities of the alloy (or physically deformed metal) at temperatures T(K) and 0(K), respectively, and $\rho_i^p(T)$ is the phonon resistivity of the ideally pure host metal, as derived from measurements on a relatively pure specimen. In the most precise measurements, particularly those extending to temperatures below 100 K, small deviations from MR have been clearly observed in many cases.[2-22] These deviations $\Delta(T)$ are usually expressed in the form

$$\Delta(T)=\rho(T)-\rho_i^p(T)-\rho(0) \qquad (2)$$

or as

$$\frac{d\Delta(T)}{dT}=\frac{d\rho(T)}{dT}-\frac{d\rho_i^p(T)}{dT}, \qquad (3)$$

where the right-hand side of Eq. (3) is simply the change in slope produced by the addition of defects.

In a considerable number of investigations the observed deviations from MR have been attributed totally, or in part, to changes in the phonon spectrum of the pure metal produced by the defects. These include investigations on various alloys[2-6] as well as cold-worked,[7-10] quenched,[11] and irradiated[10,12] metals. In nearly all of these studies the change in the phonon resistivity, associated with the phonon spectrum change, has been characterized simply by a change in the characteristic temperature θ_R used in the Bloch-Grüneisen expression[23] for $\rho_i(T)$. This expression may be written as

$$\rho_i(T)=c\,\theta_R^{-2}\,TG(\theta_R/T) \ , \qquad (4)$$

where $G(\theta_R/T)$ is a tabulated integral function[23] of (θ_R/T) and c is a constant for any particular metal. In this particular type of analysis the parameter θ_R is considered to change from θ_p for the pure metal to θ_a for the "impure" or alloyed metal, while $\rho_i(T)$ correspondingly changes from $\rho_i^p(T)$ to $\rho_i^a(T)$. Moreover, it is usually assumed that this is the only source of deviation from MR, and therefore $\Delta(T)=0$ when the more appropriate value $\rho_i^a(T)$ is used in Eq. (2), i.e.,

$$\rho(T)=\rho_i^a(T)+\rho(0) \ . \qquad (5)$$

Various investigators have predicted specific changes in θ_R to account for the apparent deviations from MR as given by Eqs. (2) and (3). In some cases, notably those analyzed by Hedgcock and Muir,[3] this particular model is reported to fit the measurements quantitatively in a most impressive manner over the entire range 4–370 K. A disturbing problem arises, however, from the fact that these reports contain seemingly irreconcilable predictions about the direction in which θ_R should change. For example, a decrease in θ_R is used to account for a negative $\Delta(T)$ function found by Das and Gerritsen,[2] a positive $\Delta(T)$ function found by Magnuson *et al.*,[12] and both a positive and negative $\Delta(T)$ function found by Hedgcock and Muir.[3] Because the various analyses used in the literature to obtain the changes in θ_R are of a diversified or unstated nature, it is not immediately obvious which reported changes are incorrect.

In the process of resolving the present unsatisfactory situation a detailed analysis of the dependence of $\Delta(T)$ and $d\Delta(T)/dT$ on the change in θ_R has been carried out within the framework of the Bloch-Grüneisen relation. Based on this analysis, major errors in two publications have been identified, and the strong support given this model by Hedgcock and Muir[3] is shown to be unwarranted. In addition a fresh assessment of the applicability of the θ_R-change model to newer experimental results is presented.

BASIC ANALYSIS

As in previous work we start with the assumption that MR is valid when the more appropriate $\rho_i^a(T)$ function is used for the phonon resistivity of the impure metal. By comparing Eqs. (2) and (5) it can be seen that the apparent deviation $\Delta(T)$ is simply equal to the change in $\rho_i(T)$ produced by the defects, i.e.,

$$\Delta(T)=\rho_i^a(T)-\rho_i^p(T) \quad . \tag{6}$$

In order to relate the apparent $\Delta(T)$ to the change in θ_R, the Bloch-Grüneisen relation is introduced into Eq. (6) by writing Eq. (4) separately for $\rho_i^a(T)$ and $\rho_i^p(T)$, noting the relationship

$$T\rho_i^a(T)=T^*\rho_i^p(T^*) \tag{7}$$

when $T/\theta_a=T^*/\theta_p$. Equation (7) is then rewritten as $\rho_i^a(T)=(\theta_p/\theta_a)\rho_i^p(T^*)$, and substituted into Eq. (6) to obtain the desired relation

$$\Delta(T)=\rho_i^p(T)\left(\frac{\theta_p\rho_i^p(T^*)}{\theta_a\rho_i^p(T)}-1\right) . \tag{8}$$

From the above equations it follows that if $\Delta\theta=\theta_a-\theta_p$ is positive then $T>T^*$; $\rho_i^p(T)>\rho_i^p(T^*)$ since $G(\theta_R/T)$ is a monotonically increasing function of T; and therefore Eq. (8) yields a negative $\Delta(T)$ function. Similarly if $\Delta\theta$ is negative it can be shown that $\Delta(T)$ must be positive. This leads to the importnat conclusion that $\Delta\theta$ and $\Delta(T)$ must have opposite signs at all temperatures.

To facilitate the calculation of $\Delta(T)$ or $\Delta\theta$ we may rewrite Eq. (8) in terms of another integral function $F(\theta_R/T)$, which is associated with the following form of the Bloch-Grüneisen relation:

$$\frac{\rho_i(T)}{\rho_i(\theta_R)}=F\left(\frac{\theta_R}{T}\right)=\frac{T}{\theta_R}\,\frac{G(\theta_R/T)}{G(1)} \quad , \tag{9}$$

where $G(1)=0.9465$. On substituting the expression for $\rho_i^p(T)$ and $\rho_i^p(T^*)$ from Eq. (9) into Eq. (8), the final result is

$$\frac{\Delta(T)}{\rho_i^p(\theta_p)}=F\left(\frac{\theta_p}{T}\right)\left(\frac{\theta_pF(\theta_p/T^*)}{\theta_aF(\theta_p/T)}-1\right) . \tag{10}$$

At high temperatures ($T>\frac{1}{2}\theta_R$) it is well known that the Bloch-Grüneisen function $F(\theta_R/T)$ varies approximately as (T/θ_R), and therefore Eq. (10) reduces to

$$\frac{\Delta(T)}{\rho_i^p(\theta_p)}\simeq-2\,\frac{\Delta\theta}{\theta_a}\,F\left(\frac{\theta_p}{T}\right) \tag{11}$$

when $\Delta\theta\ll\theta_a$. This equation may also be written explicitly in terms of $\rho_i^p(T)$ as

$$\Delta(T)\simeq-2\,\frac{\Delta\theta}{\theta_a}\,\rho_i^p(T) , \tag{12}$$

where $\rho_i^p(T)$ varies approximately as T in this range.

Similarly at low temperatures ($T<\frac{1}{10}\theta_R$) it is well known that $F(\theta_R/T)$ varies approximately as $(T/\theta_R)^5$, and therefore Eq. (10) reduces to

$$\frac{\Delta(T)}{\rho_i^p(\theta_p)}\simeq-6\,\frac{\Delta\theta}{\theta_a}\,F\left(\frac{\theta_p}{T}\right) \tag{13}$$

when $\Delta\theta\ll\theta_a$. Again, writing this equation explicitly in terms of $\rho_i^p(T)$ we obtain

$$\Delta(T)\simeq-6\,\frac{\Delta\theta}{\theta_a}\,\rho_i^p(T) \quad , \tag{14}$$

where $\rho_i^p(T)$ varies as T^5 in this range.

From Eqs. (10), (11), and (13) one may readily calculate $\Delta(T)$ at any temperature for any particular metal once $\Delta\theta$ and $\rho_i^p(\theta_p)$ are known. The required values of $F(\theta_R/T)$ may be derived from the tabulated $G(\theta_R/T)$ function using Eq. (9). Alternatively, the value of $\Delta\theta$ may be estimated once the apparent $\Delta(T)$ has been determined at a single temperature. It should also be emphasized here that Eqs. (12) and (14) lead to the conclusion that $\Delta(T)$ varies directly as $\rho_i^p(T)$ at both high and low temperatures.

In order to demonstrate the general features of the temperature dependence of $\Delta(T)$, the values of $\Delta(T)/\rho_i^p(\theta_p)$ calculated from Eq. (10) are plotted as a function of T/θ_p in Fig. 1 for a number of selected values of $\Delta\theta/\theta_p$. It is apparent that these graphs depend only on the properties of $F(\theta_R/T)$, and thus form a set of universal curves applicable to all metals.

Regarding the relationship between the slope

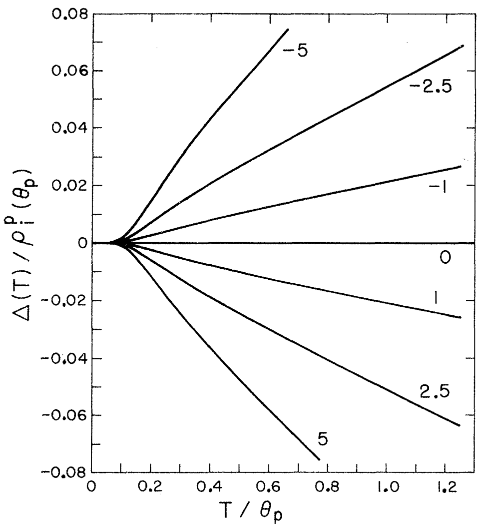

FIG. 1. Normalized departures from Matthiessen's rule, given by Eq. (10), are plotted as a function of T/θ_p for the seven different selected values of $\Delta\theta/\theta_p$ indicated on the curves in percentage form.

$d\Delta(T)/dT$ and the change in θ_R it can be seen from the graphs in Fig. 1, as well as the derivatives of Eqs. (12) and (14), that this slope will always have the opposite sign to that of $\Delta\theta$ at all temperatures, and that its absolute value will be approximately proportional to the absolute value of $\Delta\theta$. The change in slope between the pure and impure specimen, $d\rho(T)/dT - d\rho_i^p(T)/dT$, which is frequently determined in experiments, was shown to be identical to the slope of $\Delta(T)$ in both magnitude and sign in Eq. (3), and hence will also depend on $\Delta\theta$ in the above manner.

In summary then the above analysis has shown that θ_a will be $< \theta_p$ when $\Delta(T)$ and $d\Delta(T)/dT$ are positive; whereas θ_a will be $> \theta_p$ when both quantities are negative.

COMPARISON OF RESULTS

A comparison of the reported changes in θ_R given in the various publications with those of the preceding analysis reveals two discrepancies. In Das and Gerritsen's paper,[2] the negative $\Delta(T)$ component should have been attributed to an increase in θ_R on alloying; in Hedgcock and Muir's paper,[3] the negative $\Delta(T)$ and $d\Delta(T)/dT$ values in certain alloys should have been attributed to an increase in θ_R. The sources of error in these two papers, along with other important considerations, are discussed briefly below in order to clarify certain misleading arguments.

(a) Das and Gerritsen: The source of error in Das and Gerritsen's paper lies in their assumption that $\rho_i^a(T) = \rho_i^p(T)$ at temperatures below about 100 K. While it is certainly true that the difference between these two quantities [which equals the θ_R component of $\Delta(T)$] is very small at low temperatures, it may be seen from Eqs. (12) and (14) that the fractional difference $\Delta(T)/\rho_i^p(T)$ is much greater for any particular value of $\Delta\theta$ at low temperatures than at high temperatures. When this fact is taken into account it can be readily shown that their statement $[\rho_i^a(T_1)/\rho_i^a(T_2)] > [\rho_i^p(T_1)/\rho_i^p(T_2)]$ when $T_1 \ll \theta_p < T_2$ is incorrect when $\Delta(T)$ is negative, as in their case; and this in turn leads to the incorrect direction of change in θ_R. Their method of determining the change in θ_R can, in principle, give the correct answers, but is far less direct than using the relations given here.

(b) Hedgcock and Muir: The source of error in Hedgcock and Muir's paper mainly involves a lack of sensitivity in the special test that they devised to show that the observed deviations from MR can be satisfactorily taken into account by a change in θ_R alone.

The basic assumptions and procedures used in their test may be described briefly as follows: First it is assumed that MR is valid for the alloy once the change in θ_R is taken into account, and accordingly, the phonon resistivity ratio $\rho_i^a(T)/\rho_i^a(\theta_a)$ is calculated from

$$\frac{\rho_i^a(T)}{\rho_i^a(\theta_a)} = \frac{\rho^a(T) - \rho^a(0)}{\rho^a(\theta_a) - \rho^a(0)} = \frac{W^a(T) - W^a(0)}{W^a(\theta_a) - W^a(0)} , \qquad (15)$$

where $W^a(T) = \rho^a(T)/\rho^a(273)$ is determined experimentally. Similarly for the pure metal, MR is assumed since any deviations must be comparatively small, and its ratio is calculated from

$$\frac{\rho_i^p(T^*)}{\rho_i^p(\theta_p)} = \frac{W^p(T^*) - W^p(0)}{W^p(\theta_p) - W^p(0)} . \qquad (16)$$

The above two ratios are then closely fitted to the Bloch-Grüneisen function $F(\theta_R/T)$ by choosing the appropriate values for the parameters θ_p and θ_a— a procedure which obviously forces the two ratios to be the same as close as possible and makes $T/\theta_a = T^*/\theta_p$. Indeed, if their initial assumption is correct (which implies that no other sources of deviation from MR are present), one would expect the two ratios to be identical at this point. To test this supposition they have derived an expression for the residual resistivity ratio of the alloy, $W^a(0)$, by equating the right-hand sides of Eqs. (15) and (16). They then calculated $W^a(0)$ from the experimental $W(T)$ data using the chosen values of θ_a and θ_p and various selected values of the temperature T. The resulting values of $W^a(0)$ given by the equation were indeed found to agree with the measured $W^a(0)$ value to within about 1% for all values of T within the range 4–370 K.

Hedgcock and Muir suggested that the deviations from MR observed with their alloys could be satisfactorily accounted for by a change in θ_R alone. We find, on the other hand, that if the apparent $\Delta(T)$ functions shown in their Fig. 2(a) are compared with those shown in our Fig. 1, there is little or no similarity in the shapes of the graphs. Indeed some of their functions exhibit both positive and negative deviations for the same alloy, in drastic conflict with our θ_R analysis. We conclude, therefore, that the above suggestion cannot be valid, and that other sources of deviation from MR must be present for their alloys. This in turn means that their resistivity ratios calculated from Eq. (15), as well as the corresponding θ_a values, must be seriously in error.

The fact that it was possible to force the resistivity ratios given by Eqs. (15) and (16) into close agreement for the wide variety of $\Delta(T)$ curves exhibited by their alloys, demonstrates that their particular test is not significantly affected by the shape of the $\Delta(T)$ curves. Indeed, in some cases the close fit was achieved by changing θ_R in the opposite direction to that required by our analysis. A striking example of this is the case of the MgAl alloy whose ratios were made to fit by a 12% decrease in θ_R when actually its observed $\Delta(T)$ function at high temperatures corresponds crudely to a 4% increase in θ_R. Hence the test procedure used by Hedgcock and Muir to confirm the θ_R-change model was extremely insensitive and led to incorrect conclusions.

DISCUSSION

It was pointed out in the analysis of Hedgcock and Muir's work that the observed $\Delta(T)$ function could not possibly be accounted for by a change in θ_R alone. A similar conclusion has been reached by others[2,8,24] with regard to their observed $\Delta(T)$ functions; and we find on examining the remainder of the published $\Delta(T)$ functions[4,13–22,25] that the same conclusion is still valid.

Indeed, in the above work it is questionable whether there is any convincing evidence to show that a θ_R component is even partially responsible for the observed $\Delta(T)$ functions. In order to obtain such evidence it would be necessary to positively identify, and take account of, the other sources of deviation from MR. Such an approach has already been attempted by Das and Gerritsen[2] who obtained a qualitative fit to their observed $\Delta(T)$ functions by superimposing a θ_R component and a two-band $\Delta(T)$ component.[26] However, since their work a number of new theoretical sources of deviation[19,21,27] have been proposed which provide alternative explanations of their results. It should be particularly emphasized that even when $\Delta(T)$ is found to be proportional to $\rho_i(T)$ at either high or low temperatures, in accordance with the θ_R-change model [Eqs. (12) and (14)], such a dependence may be attributed to several other theoretical models. Hence at the present time there appear to be too many unknown factors to permit positive identification of a θ_R component.

The criticism which was directed at Hedgcock and Muir's calculation of θ_a and $\rho_i^a(T)$ for their various alloys may also be applied to several other publications cited here, for example, Refs. 6, 9, and 10. Because these analyses also neglect all other sources of deviation from MR, without justification, the resulting estimates of θ_a or $(\theta_p - \theta_a)$ must be considered as largely uncertain. Their reported changes in θ_R (similar to the results of Hedgcock and Muir) are found to be negative and very large, i.e., ranging from 4 to 12% per at.% solute or heavy deformation. It is possibly significant that these changes are much larger than the corresponding changes in the Debye temperature Θ_D discussed below.

Regarding the plausibility of a change in θ_R when "defects" are introduced, it is of course well established both experimentally and theoretically[28] that the phonon spectrum of a metal does change under these circumstances. For example, measurements of the lattice specific heat[28,29] and the elastic constants[30] both show that the Debye temperature Θ_D [at 0(K)] may change linearly with dilute solute concentration in either direction, and by up to 1% per at.% solute. It has also been demonstrated[8] that the increase in specific heat in the temperature range between $\frac{1}{10}\Theta_D$ and Θ_D, caused by plastic deformation, can be approximately represented within the Debye theory by a decrease in Θ_D of about 0.4% for saturation-defect concentration. It is certainly plausible, therefore, to suggest that the phonon resistivity is altered to some extent by defects, and that this change could be crudely represented by a change in θ_R.

Gregor'yants *et al.*[8] appear to be the first to have calculated a $\Delta(T)$ correction for the change in θ_R based on specific-heat measurements, and to apply this correction to their observed $\Delta(T)$ functions for plastically deformed metals. They assumed that the change in θ_R is identical to the change in Θ_D given by the specific-heat measurements, and then calculated the corresponding θ_R component of $\Delta(T)$ from the Bloch-Grüneisen relation. Unfortunately, the residual $\Delta(T)$ component, obtained by subtracting the θ_R component, could not be clearly identified with any other theoretical model, and so produced no comprehensive explanation of the measured $\Delta(T)$ function. An obvious limitation to this procedure is the substitution of the value of $\Delta\Theta_D$ for $\Delta\theta_R$, since there is no apparent theoretical reason why the two should be identical.[31]

Finally, it should be mentioned that Kagan and Zhernov[27] have performed a more rigorous theoretical analysis of the deviations (from MR) resulting from phonon spectrum changes for chemical solute. While some experimental $\Delta(T)$ functions[4,5] for alloys are qualitatively consistent with their theory, a great many others[19] do not show their predicted dependence of $\Delta(T)$ on the atomic mass ratio of the solute to solvent, or on solute concentration. Further information on phonon-assisted impurity scattering may be found in Ref. 25. At the present time, however, it appears that substantial experimental support for most theories is still lacking.

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