Thermoelectric figure of merit of composite superlattice systems

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The thermoelectric properties of systems in the form of superlattices have been studied. First, the electrical and thermal conductivities, the thermopowers, and the figures of merit of superlattice structures are given in terms of the bulk parameters of the two constituent materials for conduction both parallel and perpendicular to the superlattice axis. Second, systems in which the layers of one of the materials become sufficiently thin that their electronic properties become effectively those of a two-dimensional quantum well are considered. Numerical calculations are given for such systems with Bi_2Te_3 quantum wells separated by barriers having the parameters of bulk $Pb_{0.75}Sn_{0.25}Te$. It is shown that heat and electronic conduction through the barriers has a pronounced effect on the thermoelectric properties of the superlattice and that the figure of merit is decreased substantially for finite barrier thicknesses.

I. INTRODUCTION

Recently there has been renewed interest in finding materials with desirable thermoelectric properties, in part because of their potential for use in cooling systems and as generators.[1] The figure of merit[1] ZT provides a measure of the quality of materials for applications. To date, alloys of Bi_2Te_3 have been of the greatest interest, but only small improvements in their thermoelectric properties have been achieved in recent years. Both composite systems and bulk materials are currently of interest in the search for more desirable thermoelectrics.

An interesting proposal along these lines has been made recently by Hicks and co-workers,[2–4] who argued that the thermoelectric properties of a material can be enhanced considerably in a superlattice geometry as a result of an effectively two-dimensional density of states for the electrons. They calculated ZT for model superlattices with varying periods (well widths) in which the potential barriers of the wells were infinite and the widths of the barriers was neglected, and they found that ZT increased monotonically for decreasing well widths. On the other hand, physically we expect that nonzero barrier widths in realistic superlattice systems will significantly affect the thermoelectric properties of the superlattices, especially for narrow wells, due to transport along the barriers.

In the present work we include the effects of heat and electronic transport through barriers of nonzero thicknesses in realistic superlattices. First we consider composite systems in the form of superlattices consisting of two materials characterized by their bulk parameters. Bergman and Levy[5] have used a field-decoupling technique[6] to show for general two-component composites that the upper bound of ZT is given by the highest values of ZT of the constituent materials. Here we derive explicit results for the thermoelectric transport properties and the figures of merit of superlattice systems as functions of the layer widths for conduction both along the superlattice axis and perpendicular to it. These results explicitly give the thermoelectric transport parameters and the figures of merit of composite superlattice systems.

Second, we consider superlattice systems in which the electronic properties of one material become effectively two dimensional. We calculate numerically the thermoelectric power, the electrical conductivity, and the electronic thermal conductivity of the two-dimensional layers in the form of quantum wells with infinite barriers. The effects of nonzero thickness of the barriers between these layers on the values of ZT are obtained here, and they are shown to modify significantly the thermoelectric properties of the superlattice as compared to systems which have zero barrier thickness. In this case, ZT is less than that of the quasi-two-dimensional system with zero barrier widths for all well widths. On the other hand, we show that ZT of such a superlattice can exceed the figures of merit of each of the bulk materials characterized by bulk parameters.

These numerical calculations have been made for superlattices consisting of quasi-two-dimensional layers of Bi_2Te_3. The qualitative features of the effects of the nonzero barriers widths are not expected to depend on the choice of the barrier material. For the purpose of discussing this effect we choose barriers characterized by the bulk parameters of $Pb_{0.75}Sn_{0.25}Te$. Such superlattices are of current practical interest,[2–4,7] and the parameters for them are known relatively well.

In Sec. II the equations for thermoelectric transport are summarized. In Sec. III the thermoelectric transport properties of composite superlattice systems are derived in terms of the bulk properties of the materials. In Sec. IV the properties of superlattices consisting of layers with two-dimensional electronic properties and barrier layers having nonzero widths are calculated.

II. THERMOELECTRIC TRANSPORT EQUATIONS

The macroscopic transport equations for thermoelectric materials relate the electric current density $\mathbf{J}_e$ and thermal current density $\mathbf{J}_s$ to the electric field $\mathbf{E}=-\nabla\phi$

and temperature gradient ∇T, where ϕ is the electric potential. It is convenient to write these equations in a matrix form in which all of the matrix elements have the same units:[5]

$$J=S\nabla\psi\ , \tag{1}$$

where

$$J\equiv\begin{bmatrix}-J_e/e\\-J_s/k\end{bmatrix}\ , \tag{2}$$

$$\nabla\psi\equiv\begin{bmatrix}\nabla(e\phi)\\\nabla(kT)\end{bmatrix}\ , \tag{3}$$

$$S\equiv\begin{bmatrix}\dfrac{\sigma}{e^2} & \dfrac{\sigma\alpha}{ek}\\[2ex]\dfrac{\sigma\alpha}{ek} & \dfrac{\gamma}{k^2T}\end{bmatrix}\ . \tag{4}$$

Here the electrical conductivity σ, the thermal conductivity at zero electric field γ, and the thermoelectric power α are in general 3×3 matrices in the Cartesian coordinates. They satisfy

$$\mathbf{J}_e=\sigma\mathbf{E}\quad\text{for }\nabla T=0\ , \tag{5}$$

$$\mathbf{E}=\alpha\nabla T\quad\text{for }\mathbf{J}_e=0\ , \tag{6}$$

$$\gamma=\kappa+T\sigma\alpha^2\ , \tag{7}$$

where κ is the usual thermal conductivity at zero electric current.

The thermoelectric figure of merit ZT is defined as

$$ZT\equiv\frac{S_{12}^2}{\det S}=\frac{\Delta}{1-\Delta}=\frac{\sigma\alpha^2T}{\kappa}\ , \tag{8}$$

where

$$\Delta=\frac{S_{12}^2}{S_{11}S_{22}}=\frac{\sigma\alpha^2T}{\gamma} \tag{9}$$

and

$$\det S=\frac{\sigma\kappa}{k^2e^2T}\ . \tag{10}$$

Note that ZT is a monotonic function of parameter Δ, and thus either quantity may be used as a quality factor for thermoelectric materials.[5]

III. COMPOSITE SUPERLATTICE SYSTEMS

Here we obtain the thermoelectric transport properties of composite systems which have the form of superlattices composed of layers of materials A and B with layer thicknesses a and b, respectively, in terms of their corresponding bulk parameters. The superlattice growth direction is taken to be the x direction. For simplicity, we assume that both materials are isotropic, and therefore in each material σ, α, and γ are constants. We use the subscripts a, b, and C to label quantities in the material A, in material B, and in the effective composite superlattice system, respectively. The subscript M is used to represent the greater of the values of a given parameter in the two bulk materials A and B.

A. Current in the growth direction

In this case the current J flows perpendicular to the planes of the layers, and it is uniform through the system. The potential drop between $x=0$ and $x=a+b$ is from Eq. (1):

$$\int_0^{a+b}\nabla\psi\,dx=\int_0^{a}S_a^{-1}J\,dx+\int_a^{a+b}S_b^{-1}J\,dx$$
$$=J(S_a^{-1}a+S_b^{-1}b)\equiv JS_C^{-1}(a+b)\ . \tag{11}$$

Thus the inverse of the effective thermoelectric transport matrix S_C^{-1} of the composite system is given by

$$S_C^{-1}=\frac{S_a^{-1}a+S_b^{-1}b}{a+b}\ . \tag{12}$$

From Eq. (12) for the transport coefficients we obtain

$$\sigma_C=\left[\frac{\sigma_a\kappa_a}{a}\right](\sigma_a+q\sigma_b)W\ , \tag{13}$$

$$\gamma_C=\left[\frac{\sigma_a\kappa_a}{a}\right](\gamma_a+q\gamma_b)W\ , \tag{14}$$

$$\alpha_C=\frac{\sigma_a\alpha_a+q\sigma_b\alpha_b}{\sigma_a+q\sigma_b}<\alpha_M\ . \tag{15}$$

The parameter Δ is given by

$$\Delta_C=\frac{T(\sigma_a\alpha_a+q\sigma_b\alpha_b)^2}{(\gamma_a+q\gamma_b)(\sigma_a+q\sigma_b)}=\frac{(\sqrt{\Delta_a}+\sqrt{h_\sigma h_\gamma\Delta_b})^2}{(1+h_\sigma)(1+h_\gamma)}$$
$$<\Delta_M\ . \tag{16}$$

Here α_M is the greater of the thermopowers of the two bulk systems (α_a,α_b). The parameters q, W, and h are

$$q\equiv\frac{b(\det S_a)}{a(\det S_b)}=\frac{b\sigma_a\kappa_a}{a\sigma_b\kappa_b}\ , \tag{17}$$

$$W\equiv(a+b)[(\gamma_a+q\gamma_b)(\sigma_a+q\sigma_b)$$
$$-T(\sigma_a\alpha_a+q\sigma_b\alpha_b)^2]^{-1} \tag{18}$$

and

$$h_\sigma=q\frac{\sigma_b}{\sigma_a}\ ,\quad h_\gamma=q\frac{\gamma_b}{\gamma_a}\ . \tag{19}$$

B. Current perpendicular to the growth direction

In this case the current flows along the planes of the superlattice in a direction that we denote as y, and care must be taken to define properly the thermoelectric transport matrix S for the composite system. Here the current density is a function of position x along the superlattice axis. We seek the average of the current density $\langle J\rangle$ over a large cross-sectional area perpendicular to the direction of the flow:

$$\langle J\rangle=S_C\langle\nabla\psi\rangle=S_C\nabla\psi\ . \tag{20}$$

The second step in Eq. (20) results because each cross section perpendicular to the current flow is an equipotential and isothermal plane.

Because the potential drop in materials A and B between positions $y=0$ and y_0 is independent of x,

$$\int_0^{y_0}\nabla\psi\,dy=\int_0^{y_0}S_a^{-1}J_a dy=\int_0^{y_0}S_b^{-1}J_b dy \tag{21}$$

or

$$J_b=S_bS_a^{-1}J_a\ . \tag{22}$$

Thus

$$\langle J\rangle=\frac{aJ_a+bJ_b}{a+b}=\frac{(aS_a+bS_b)\nabla\psi}{a+b} \tag{23}$$

and

$$S_C\equiv\frac{\langle J\rangle}{\nabla\psi}=\frac{aS_a+bS_b}{a+b}<S_M\ . \tag{24}$$

Here S_M is the greater of the values S_a and S_b corresponding to the two bulk materials, and the relation holds for each of the matrix elements of S. From Eq. (24), for transport coefficients with current in the y direction, we obtain

$$\sigma_C=\frac{a\sigma_a+b\sigma_b}{a+b}<\sigma_M\ , \tag{25}$$

$$\gamma_C=\frac{a\gamma_a+b\gamma_b}{a+b}<\gamma_M\ , \tag{26}$$

$$\alpha_C=\frac{a\sigma_a\alpha_a+b\sigma_b\alpha_b}{a\sigma_a+b\sigma_b}<\alpha_M\ . \tag{27}$$

From these results, we find

$$\Delta_C=\frac{(\sqrt{\Delta_a}+\sqrt{f_\sigma f_\gamma\Delta_b})^2}{(1+f_\sigma)(1+f_\gamma)}<\Delta_M\ , \tag{28}$$

where

$$f_\sigma\equiv\frac{b\sigma_b}{a\sigma_a}\ ,\quad f_\gamma\equiv\frac{b\gamma_b}{a\gamma_a}\ , \tag{29}$$

and thus the figure of merit is

$$Z_CT=\frac{\Delta_C}{1-\Delta_C}<Z_MT\ , \tag{30}$$

$$Z_CT=\frac{(\sqrt{Z_aT}+\sqrt{f_\sigma f_\kappa Z_bT})^2}{(1+f_\sigma)(1+f_\kappa)+(\sqrt{f_\sigma Z_aT}-\sqrt{f_\kappa Z_bT})^2}\ , \tag{31}$$

where

$$f_\kappa\equiv\frac{b\kappa_b}{a\kappa_a}=f_\gamma\left[\frac{1-\Delta_b}{1-\Delta_a}\right]\ . \tag{32}$$

We see from Eqs. (16) and (30) for current flow either along the superlattice axis or perpendicular to it that ZT of the composite superlattice system is always less than the maximum of $(Z_aT,\ Z_bT)$, the figures of merit of the bulk materials A and B, as shown earlier for general two component composite systems.[5]

We note that in both current directions ZT depends on the layer widths only through the ratio b/a. In addition, we find explicitly for both directions that the following interesting relations holds between the thermopowers for the composite system and those for the two bulk systems:

$$\frac{\alpha_C-\alpha_b}{\alpha_a-\alpha_b}=\frac{\left[\frac{\gamma_C}{\sigma_C}-\frac{\gamma_b}{\sigma_b}\right]}{\left[\frac{\gamma_a}{\sigma_a}-\frac{\gamma_b}{\sigma_b}\right]}\ , \tag{33}$$

which was obtained earlier[5] for general two-component composite systems.

IV. NUMERICAL CALCULATIONS FOR QUASI-TWO-DIMENSIONAL SUPERLATTICES

Here we consider the effects of the nonzero widths of the barriers separating the quasi-two-dimensional electronic layers of realistic superlattices. We give numerical calculations for the thermoelectric properties of a model superlattice system for the two directions of transport. For transport perpendicular to the superlattice axis, we consider systems in which the layers of material A are thin enough so that their electronic properties behave as effective two-dimensional quantum wells. In order to facilitate comparison with previous results,[2] we take the quantum-well material to be Bi_2Te_3.

We are interested in the qualitative effects of the nonzero barrier widths, and for the present purposes we will take the barrier material to be characterized by its bulk parameters for all well widths. That is, we will neglect the modifications of the properties of the barrier layers for small widths. Further, we expect that the qualitative features of the nonzero barrier widths do not depend on the choice of barrier material. For the present discussion we choose the barrier material B to have the properties of $Pb_{0.75}Sn_{0.25}Te$, because Bi_2Te_3/$Pb_{0.75}Sn_{0.25}Te$ superlattice systems are being grown and are of practical interest,[7] and also their thermoelectric transport coefficients are relatively well known.[8] The thermoelectric transport coefficients of $Pb_{0.75}Sn_{0.25}Te$ are taken from the bulk room-temperature measurements of Rosi, Hockings, and Lindenblad,[8] and are $\sigma_b=1.176\times10^3/\Omega\,\mathrm{cm}$, $\kappa_b=2.046$ W/m K, $\alpha_b=108$ μV/K, and $Z_bT=0.20$. The corresponding values for bulk Bi_2Te_3 are $\sigma_a=0.588\times10^3/\Omega\,\mathrm{cm}$, $\kappa_a=1.8$ W/m K, $\alpha_a=240$ μV/K, and $Z_aT=0.56$.

For later comparison, we first calculate the figure of merit ZT of the superlattice for the case in which the current is in the direction parallel to the axis of the superlattice. For this case the quantization of the carriers in the Bi_2Te_3 layers should not have a significant effect on the transport properties, and we will assume to first approximation that the transport parameters are given by the bulk values for both materials. That is, physically this situation is taken to be the same as that described in Sec. III. The results for ZT for this case are shown by the solid line in Fig. 1 as a function of the ratio of layer

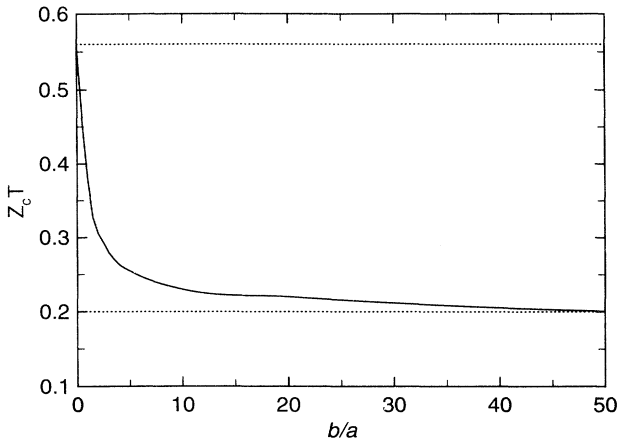

FIG. 1. The thermoelectric figure of merit $Z_C T$ of the superlattice system $Bi_2Te_3/Pb_{0.75}Sn_{0.25}Te$ as a function of ratio of the layer widths b/a for the case in which current flows along the superlattice growth direction. Here both materials in the superlattice are characterized by bulk transport parameters. The dotted lines indicate the figures of merit of the two bulk materials, with the upper line corresponding to Bi_2Te_3 and the lower to $Pb_{0.75}Sn_{0.25}Te$.

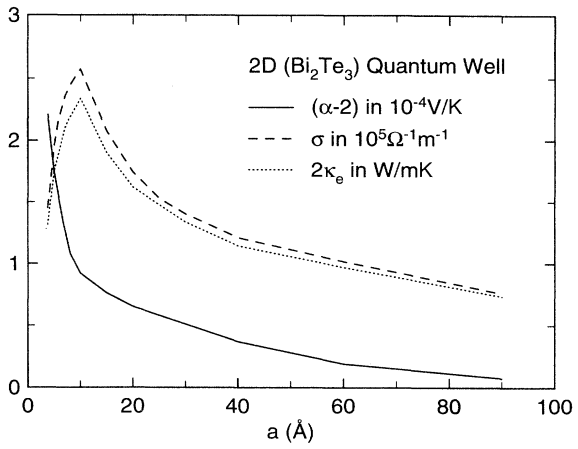

FIG. 2. The electrical conductivity σ, the electronic thermal conductivity κ_e, and the thermoelectric power α of a Bi_2Te_3 quantum well as a function of the well width a calculated as described in the text.

thicknesses b/a. The dotted lines are for the bulk materials Bi_2Te_3 (upper) and $Pb_{0.75}Sn_{0.25}Te$ (lower). The solid curve lies between the dotted lines, indicating that the ZT of the composite system for transport in this direction is less than the greater of the values of Z_aT and Z_bT for the individual bulk components for all well widths, which is a concrete example of the analytical result in Eq. (16).

Next we consider the situation in which the current flows perpendicular to the superlattice axis. In this case we take the layers of Bi_2Te_3 to behave as effective two-dimensional quantum wells for electronic transport along the wells. As a first approximation we calculate the values of α, σ, and γ for the Bi_2Te_3 layers from the two-dimensional density of electronic states, as done in Ref. 2. That is, the electronic states are taken to be those appropriate for the lowest subband of a quantum-well system with infinite potential barriers,[9] and α, σ, and γ are evaluated at the chemical potential (i.e., the density) for which the figure of merit of the quasi-two-dimensional layer is a maximum. The lattice thermal conductivity κ_{ph} of the quantum-well layers is taken to be the bulk value for Bi_2Te_3 (1.5 $W\,m^{-1}\,K^{-1}$) for well widths larger than the thermal mean free path $l=10$ Å, and for well widths less than 10 Å it is taken to be

$$\kappa_{ph}=\tfrac{1}{3}C_v v l \ , \tag{34}$$

with $l=a$, the well width. Here C_v is the heat capacity, and v the velocity of sound. This estimate of κ_{ph} for small well widths is used in Ref. 2 to represent in an approximate way the increased scattering from the interfaces of the quantum well.

The transport coefficients of the quasi-two-dimensional Bi_2Te_3 layers calculated in this way are shown in Fig. 2 as functions of the well width. The decreases of the electrical conductivity σ and electronic thermal conductivity κ_e for $a<10$ Å shown in Fig. 2 are due mainly to the change of the chemical potential in well widths. The chemical potential is evaluated at the density which gives the largest figure of merit of the layer, and it is influenced by the modification of the phonon thermal conductivity for well widths $a<10$ Å given in Eq. (34). The thermoelectric power α is found to increase continuously as the width decreases.

The ZT of the superlattices is calculated in Eq. (31) by

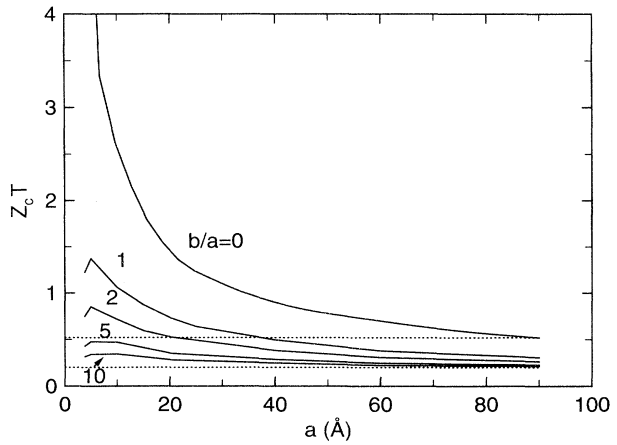

FIG. 3. The thermoelectric figure of merit $Z_C T$ of superlattice systems composed of quasi-two-dimensional quantum wells of Bi_2Te_3 and barriers having the properties of bulk $Pb_{0.75}Sn_{0.25}Te$ as a function of ratio b/a, where a is the thickness of the Bi_2Te_3 layers, and b is the thickness of the $Pb_{0.75}Sn_{0.25}Te$ layers for the case in which current flows perpendicular to the superlattice growth direction. The dotted lines indicate the figures of merit of the two bulk materials, with the upper line corresponding to Bi_2Te_3 and the lower to $Pb_{0.75}Sn_{0.25}Te$.

using the values of α, γ, and σ calculated in this way for the Bi_2Te_3 layers and using the bulk parameters α, γ, and σ for the $Pb_{0.75}Sn_{0.25}Te$ barriers, and the results are shown in Fig. 3 as a function of a for several b/a. The dotted lines correspond to the bulk Bi_2Te_3 and $Pb_{0.75}Sn_{0.25}Te$ materials. In the case in which the barrier layers have zero thickness, $b/a=0$, we recover the results of Hicks and Dresselhaus,[2] which neglect the barrier widths in determining ZT and which give a dramatically increasing ZT for decreasing well widths. For finite barrier thicknesses b/a, on the other hand, the figure of merit is considerably reduced from these values. Physically, this reduction occurs because for nonzero barrier widths thermal and electrical currents flow along the barriers as well as the wells. The thermal current through the barrier constitutes a kind of parasitic channel with respect to the quantum wells, and decreases ZT. For large barrier widths and $b/a \gg 1$, ZT goes over to the value for the bulk barrier material.

In the calculations done here ZT develops a weak maximum for well widths near 10 Å. The origin of this maximum is the same as those for σ and κ_e in Fig. 2. These features result from the modification[2] of the phonon thermal conductivity given in Eq. (34) for small well widths to account for interfacial phonon scattering. It should be noted that this modification is a rather crude approximation for real physical systems. We have also done calculations in which the phonon thermal conductivity in the quantum wells is taken to be its bulk value ($\kappa_{ph}=1.5\ \mathrm{W\,m^{-1}\,K^{-1}}$) for all well widths, and in this case the weak maximum does not appear for $a<10$ Å. Thus ZT in the region of 10 Å is sensitive to the choice of the κ_{ph}, which is not well understood for superlattice systems.

From the results in Fig. 3 we see (i) that ZT for a composite superlattice system can be increased modestly above that of the maximum of the constituent bulk materials as a result of the two-dimensional character of the electronic properties in one of the materials for small well widths, and (ii) that ZT of the superlattice is substantially less than that of the quasi-two-dimensional material with zero barrier thicknesses for all well widths. We see that the nonzero barrier width has a significant effect in determining ZT of superlattice systems. The precise value of ZT for a given well width a and ratio b/a depends on the choices of materials in the superlattice.

For clarity of comparison with previous results,[2] the calculations above have used infinite potential barriers for the quasi-two-dimensional electronic properties of the quantum-well layers in the superlattices. In realistic systems with finite potential barriers, however, for thin enough layers electronic carrier tunneling between the layers begins to become important. The effects on the thermoelectric power of superlattices of such carrier tunneling have been studied previously.[10,11] These effects are not included in the results given here for ZT. In general terms, we expect that such carrier tunneling will smooth out the two-dimensional steps in the density of states of the quantum well, and will further reduce the figure of merit from that obtained here. See the "Note added in proof."

In summary, we have first given explicit results for thermoelectric transport properties and figures of merit of superlattices which have layers that are thick enough that they can be characterized by bulk transport parameters. We find that for transport either along or perpendicular to the superlattice axis the figures of merit of such composites are less than the maximum of those for the two bulk materials for both directions of transport. Secondly, in the case in which the layers of one of the materials are thin enough to show effectively two-dimensional electronic properties, we find that the figure of merit of the superlattice for transport perpendicular to the superlattice axis can be enhanced to values above those for either of the bulk systems, but that it is decreased below that for the two-dimensional system with zero barrier widths due to heat and electronic transport through the barrier layers.

Note added in proof. In subsequent work the effects of carrier tunneling on ZT have been considered.[12] There the layers of the superlattice are taken to be of the same material with potential offsets between them.

ACKNOWLEDGMENT

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