FIG. 10. This thermocouple circuit is used to explain the minus sign in the Kelvin relation (70).

thermoelectric current. This current increase would result in still further cooling of the left junction and further heating of the right, and so on. Once started with a minute ΔT this thermocouple device would thus generate an increasing current and would furthermore cool the left junction without any external interaction. This being impossible we conclude that if the relative thermopower S_{XR} is positive, the left-hand junction in Fig. 10 must become a heat source so that with the current I crossing the X-R junction in the direction from X to R the Peltier heat must be negative. This explains the minus sign in Eq. (70).

The relations between the various thermomagnetic coefficients (Hall, Nernst, Ettingshausen, Righi-Leduc) have been found by Callen.[13]

G. ANISOTROPY OF THERMOELECTRIC EFFECTS

According to Eq. (21) a particle current density J_e flowing in an isothermal rod has associated with it an entropy current density given by $J_s = S^* J_e$, in which the transport entropy per particle S^* depends on the chemical nature of the phase and on the temperature. The value of this parameter S^* for a given kind of particle (electron, say) in a given phase is determined by the detailed way in which the particle is scattered as it passes through the atomic lattice of the phase. One would not be too surprised, therefore, to find that in a single crystal the value of S^* for a given charge carrier depends in general upon the crystallographic direction in which the carrier moves or drifts. Since the absolute thermoelectric power of a phase is determined by S^* it would follow that the thermoelectric properties of a (noncubic) single crystal would vary with crystallographic direction. This is in fact the case, and a considerable amount of thermoelectric data is available on such pure metal single crystals as zinc, cadmium, antimony, bismuth, tin, and magnesium.[14] We wish to discuss next the theoretical aspects of thermoelectric anisotropy. We begin by postulating a tensor formulation of the fundamental thermoelectric equations applicable to any crystalline or otherwise non-isotropic as well as nonhomogeneous medium. We then

[13] H. B. Callen, Phys. Rev. 85, 16 (1952).
[14] W. Meissner, *Handbuch der Experimentalphysik* (Leipzig, 1935), vol. XI, pt. 2.

apply the general equations to special crystal systems; of particular importance is the application to "uniaxial" crystals, since these are the ones most extensively studied experimentally. The applications of the general theory lead to the Kelvin symmetry relations and to Bridgman's "internal Peltier effect." Finally, we compare our formulation with those of Kelvin, Bridgman, Ehrenfest and Rutgers, Meissner, Kohler, and Meixner.

1. The General Equations for Anisotropic Media

We use as a starting point the combination of relations (21) and (X-8), namely[15]

$$\mathbf{J}^s = S^* \mathbf{J}^e - (\kappa/T) \boldsymbol{\nabla} T. \qquad (72)$$

In setting up the general equations *we make the assumption that each component of the entropy current density J_i^s is a linear function of the components J_j^e, of particle current density and of the components $\nabla_j T$ of the temperature gradient, with i, $j = 1,2,3$. The temperature T and the electrochemical potential $\bar{\mu}$ are considered as continuous and differentiable functions of position (x_1, x_2, x_3) within each phase. If an electrical current flows across a boundary between two media, there will be cases (as mentioned in Example 6 of Appendix B) in which the electrochemical potential cannot be defined *within* the junction. In such cases, however, the finite jump in $\bar{\mu}$ across the junction can be defined and one needs only to use the appropriate boundary conditions for $\bar{\mu}$; otherwise such cases introduce no particular difficulties. The relation (72) is thus replaced by the three equations[16]

$$J_i^s = S_{ij}^* J_j^e - (\kappa_{ij}/T)(\partial T/\partial x_j), \quad i, j = 1, 2, 3, \quad (73)$$

in which the quantities S_{ij}^* form the *transport entropy matrix* and the κ_{ij} form the *heat conductivity matrix*. We emphasize the fact that the equations (73) are postulates, reasonable extensions of the isotropic Eq. (72), and that their validity must be checked by experiment. At the present time there is available only information on crystals of comparatively high symmetry, to which the simpler Kelvin and Kohler symmetry relations are supposedly applicable. Although the Kelvin-Kohler relations appear to be quite well satisfied by available data on such crystals, there is still need for further and more extensive measurements on single crystals over large temperature ranges.

[15] We shall hereafter write the subscripts s and e in (72) as superscripts to make room for the subscript indices i and j.
[16] The presence of two identical subscripts indicates a summation. Thus (73) is shorthand notation for the three components

$$J_1^s = S_{11}^* J_1 + S_{12}^* J_2 + S_{13}^* J_3 - \frac{1}{T}\left(\kappa_{11}\frac{\partial T}{\partial x_1} + \kappa_{12}\frac{\partial T}{\partial x_2} + \kappa_{13}\frac{\partial T}{\partial x_3}\right),$$

$$J_2^s = S_{21}^* J_1 + S_{22}^* J_2 + S_{23}^* J_3 - \frac{1}{T}\left(\kappa_{21}\frac{\partial T}{\partial x_1} + \kappa_{22}\frac{\partial T}{\partial x_2} + \kappa_{23}\frac{\partial T}{\partial x_3}\right),$$

$$J_3^s = S_{31}^* J_1 + S_{32}^* J_2 + S_{33}^* J_3 - \frac{1}{T}\left(\kappa_{31}\frac{\partial T}{\partial x_1} + \kappa_{32}\frac{\partial T}{\partial x_2} + \kappa_{33}\frac{\partial T}{\partial x_3}\right).$$