THE EFFECT OF TENSION ON THE THERMOELECTRIC PROPERTIES OF METALS

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Summary

Measurements have been made on 11 different metals of the change in thermoelectric power accompanying elastic tensile strain. The measurements were made over the temperature range 20–400 °C on specimens of known purity. There is evidence that the magnitude of the general effect is dependent upon the purity of the specimen. The results obtained with gold differ considerably from those found by another observer.

New approximate values of the general coefficients, which describe the first-order change in thermoelectric power for isotropic metals under all types of elastic strain, have been computed using the results obtained and the only available similar low pressure data. The new values suggest that recent conclusions regarding the position of the Fermi level for gold, silver, and copper require modification.

I. Introduction

It has long been known (e.g. Thomson 1856) that tensile stress produces changes in the thermoelectric properties of metals. This phenomenon has been investigated in some detail by Cohn (1879), Meyer (1896), Maclean (1900), Baedecker and Vehrigs (1914), Bridgman (1918), and Smith (1925). In much of this earlier work the effect of plastic deformation, which may produce effects of the same order of magnitude but sometimes of opposite sign to that produced by elastic deformation (Thomson 1856), was not fully distinguished from the latter (Borelius 1935). More recently Crussard (1948) made quantitative measurements of the change in thermoelectric power caused by pure elastic tensile strain on four pure metals at about 100 °C.

Within the elastic range it is possible to determine the effect of any type of strain on thermoelectric properties, to a first order, from general coefficients. The observed effect is, of course, dependent upon the relative directions of the temperature gradient and strain vectors. The coefficients applicable to isotropic metals may be found by a consideration of the observed effects of longitudinal tension and hydrostatic pressure on suitable metal specimens. Smit (1952) utilizes such coefficients in a discussion of the influence of elastic shear strains on the conductivity and thermoelectric power of cubic metals.

This paper reports measurements of the effect of elastic tensile strain on 11 different metals of known purity over the temperature range 20–400 °C. From the results obtained approximate values of the isotropic general strain coefficients for some of the metals investigated are deduced.

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II. Experimental Method

The principle of the method of investigation was the same as Crussard's (1948), measurements being made of the e.m.f. generated by a thermocouple formed from a continuous single metal wire so arranged that one arm was subjected to a longitudinal tension while the other was mechanically free. The apparatus is shown schematically in Figure 1. The cold junction temperature was maintained at 20 ± 1 °C, while the mean accuracy of the hot junction temperature control was approximately ± 4 °C. The e.m.f. was measured with a potentiometer having a least count of $0 \cdot 1$ μV, usually in conjunction with a galvanometer amplifier (Wylie 1951). By this means e.m.f. changes could be measured to about $\pm 0 \cdot 002$ μV.

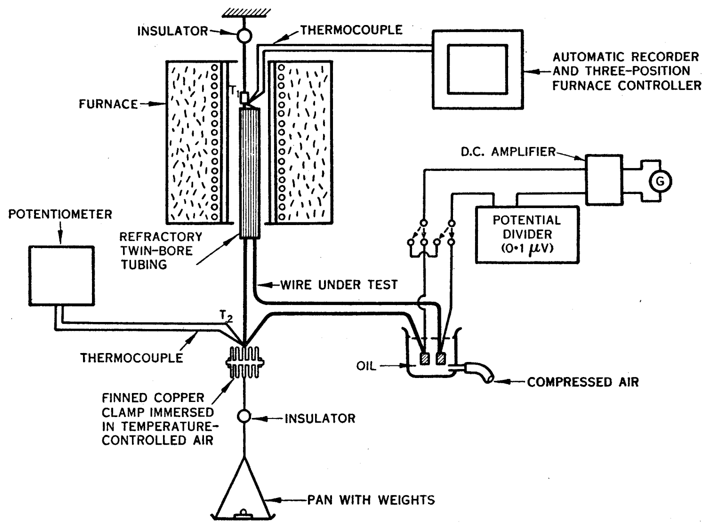

Fig. 1.—Method of measuring a small thermal e.m.f. due to strain.

For each specimen measurements were made at a series of hot junction temperatures, and at each such temperature a definite loading procedure was followed in order to eliminate from the results the effects of plastic deformation which was sometimes present. Measurements were made in succession of the e.m.f.'s E_{W+W_0}, E_{W_0}, E_{2W+W_0}, E_{W+W_0} etc. where W is an incremental load, fixed for any specimen, and W_0 is the weight of the cold junction unit etc. ; the e.m.f. corresponding to a stress intensity $(nW+W_0)$ was taken to be given by

$$\sum_{r=1}^{r=n} (E_{rW+W_0} - E_{(r-1)W+W_0}).$$

This procedure had the advantage over one in which readings were taken as the stress was progressively reduced from the maximum loading used that the measurements were not left incomplete in the event of the wire breaking. Control experiments showed that the e.m.f. obtained by the two methods agreed to within the experimental error, indicating that within the limits of stress intensity used any work hardening of the specimen produced negligible change in the thermal e.m.f. due to elastic strain. Although any effects due to creep or creep recovery appeared to be negligible, a precautionary period of approximately 5 min was allowed to elapse between readings for reproducibility; this also allowed the dissipation of heat generated in switch contacts.

The sequence of hot junction temperatures followed for most specimens was 100, 200, 300, 400, 50, 150, 250, 350 °C, thus revealing any change in the characteristics of the specimen with temperature or successive loadings. Measurements were also usually made subsequently at other temperatures, particularly if the earliest readings were inconsistent with those obtained later; this effect was attributed to straightening of the wire specimens.

TABLE 1

METALS TESTED

Metal	Origin	Mechanical Condition	Purity or Analysis* (quantities in %)
Copper I	J,M	Annealed	99·999
Silver I	,,	,,	99·999
Silver II	Commercial	,,	~99·94; traces Cu, Hg
Gold I	J,M	,,	99·99(+)
Gold II	Commercial	,,	~99·93; Ag (0·05), Fe (0·01), trace Cu
Gold III	,,	,,	~99·91; Ag (0·06), Fe (0·02), strong trace Zn, trace Cu
Gold IV	,,	,,	~99·90; Ag (0·07), Fe (0·02), trace Cu
Platinum	J,M	,,	99·999
Palladium	,,	,,	99·995
Nickel	,,	,,	99·99
Aluminium	Commercial	,,	~99·58; Si (0·09), Fe (0·03), Cu (0·01), Mn (0·01), Ti (0·01)
Titanium	,,	,,	Strong traces Fe, Mn, traces Mg, Si
Molybdenum	,,	,,	~99·95; trace Si, faint trace to trace Fe
Iron I	,,	(i) Cold drawn (ii) Annealed	Undrawn sample; Mn (0·2), Cu (0·15), Ni (0·1), traces (~0·03) Cr, Sn, As, C
Iron II	,,	(i) As received (ii) Annealed	Mn (0·5), Ni (0·1), Cr (0·1), Cu (0·1), C (0·09)
Tungsten	,,	As received	Traces Mo, Si

* Any impurity concentration which was less than or equal to the spectrographic level of "faint trace" has been neglected in the table.

III. SPECIMENS

Details of the metals examined, their chemical purity or major impurities or both, and the physical state of the specimens when tested, are given in Table 1. The materials marked J, M were supplied by Johnson, Matthey and Co. Limited, of London, as spectrographically pure. The specimens were annealed by electrical heating *in vacuo*.

IV. Experimental Results

The results are set out graphically in Figures 2 and 3, where the summed e.m.f. increments, E, are plotted as ordinates and the corresponding temperature differences between hot and cold junctions, T_1–T_2, as abscissae; each curve

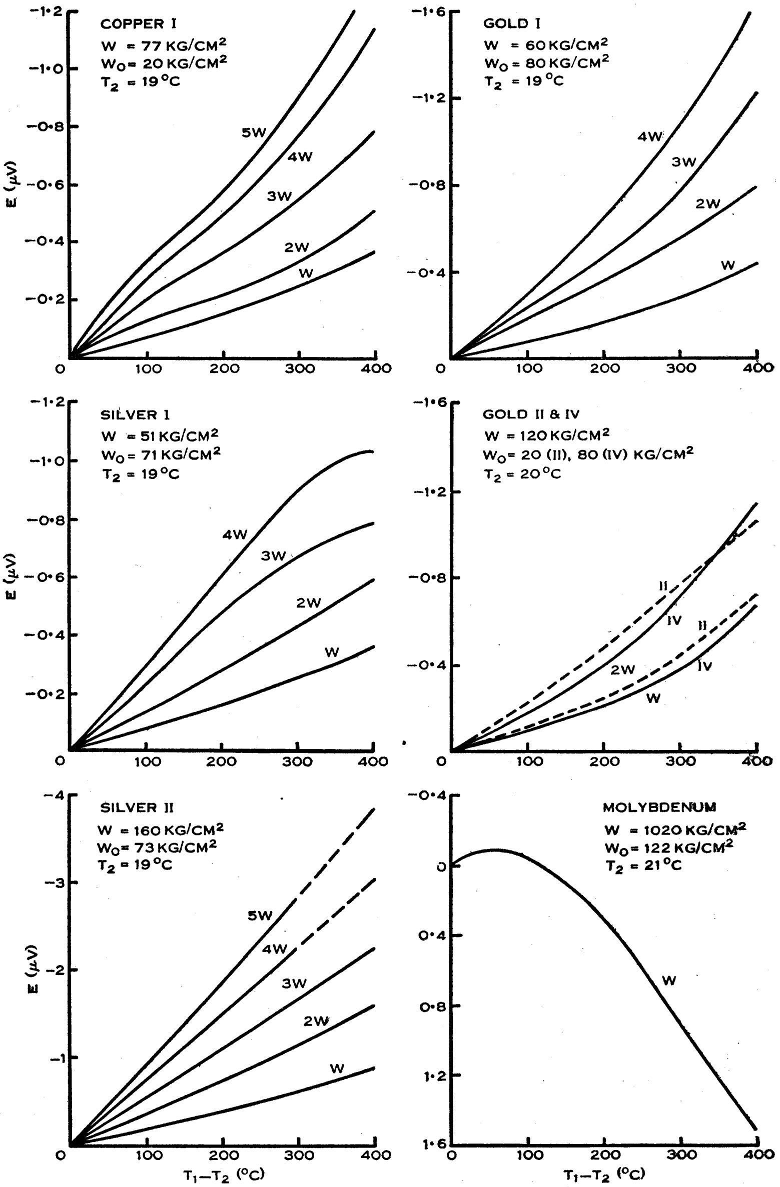

Fig. 2.—E.M.F. of strain thermocouples as a function of the temperature difference between hot and cold junctions for particular stress intensities.

refers to a multiple of the basic stress intensity increment W. The magnitude of both W and W_0 is noted in each figure together with T_2, the mean cold junction temperature.

The sign convention used is that the e.m.f. is taken to be positive if the current flow on completion of the thermoelectric circuit is from the free wire to the stressed wire through the hot junction. The scatter of the plotted points

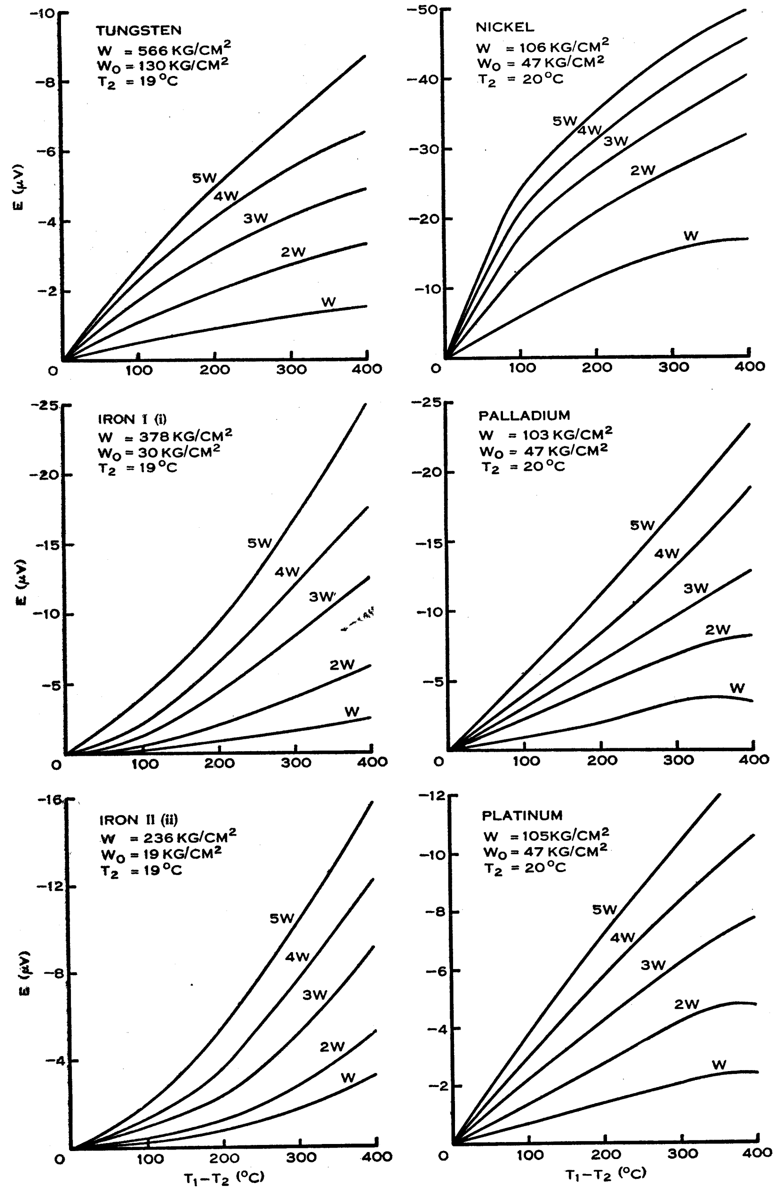

Fig. 3.—E.M.F. of strain thermocouples as a function of the temperature difference between hot and cold junctions for particular stress intensities.

is summarized in Table 2, where the averages of the r.m.s. deviation from each curve are listed. It was found, usually, that the numerical deviation from any given curve was approximately independent of temperature.

Certain of the metals tested require special comment.

Silver II.—The dotted lines in Figure 2 refer to extrapolation into the region where the combination of temperature and stress was sufficient to cause rupture.

Gold.—Plots of the results obtained for gold III are not given as they are similar to those for gold IV. However, the stress range employed was approximately the same in all the gold specimens and the more important results are summarized in Table 3.

Titanium.—The results showed very great scatter, hence it is only possible to give a rough estimate of one of the results for this metal (see Table 3, where $W_0=23$ kg/cm^2 and $t_{max.}=1440$ kg/cm^2).

Molybdenum.—Although a series of readings were taken corresponding to a stress of $W/2$, the ratio of scatter to nominal ordinate was so large that smoothed data can be given for the higher stress only.

Tungsten.—The results given in Figure 3 were obtained on a specimen as supplied, electrical annealing *in vacuo* causing prohibitive embrittlement.

TABLE 2

RANDOM ERRORS OF THE MEASUREMENTS SHOWN IN FIGURES 2 AND 3

Metal	Av. r.m.s. Deviation (μV)	Metal	Av. r.m.s. Deviation, (μV)
Copper I	0·05	Tungsten	0·2
Silver I	0·06	Iron I	0·5
Silver II	0·07	Iron II	0·4
Gold I	0·05	Palladium	1·4
Gold II and IV	0·03	Platinum	0·25
Molybdenum	0·09	Nickel	1·0

Iron.—Before any satisfactory experiments could be carried out on iron wire it was found necessary to make the furnace winding bifilar in order to reduce the internal alternating magnetic field, as any small torsional strain imposed on the test specimen during mounting makes the magnetic susceptibility of the material anisotropic (Dromgoole 1952). In an alternating magnetic field an induced voltage is therefore produced between the ends of the specimen, leading to an unsteady galvanometer spot.

Iron I.—Annealing produced effects which were not reproducible in magnitude, but it is possible to make a few general remarks on the qualitative form of the change.

On annealing, the e.m.f. became predominantly positive and non-linear in its relation to stress, at constant junction temperatures. The e.m.f. generally increased as the load increased, reached a maximum, then decreased. The variation with temperature at constant stress was similar, the e.m.f. increased as the temperature difference increased, reached a relatively poorly defined maximum at roughly 300 centigrade degrees, then decreased.

Iron II.—The curves given in Figure 3 are based on readings obtained on an annealed specimen. Readings taken on an unannealed specimen were practically identical; this was not unexpected in this case since the general mechanical softness of the metal as received suggested that it had already been annealed.

Aluminium.—Measurements on the sample of aluminium were restricted to temperatures between 20 and 150 °C because of the relatively low elastic limit of the material at higher temperatures. It was not found possible to obtain reproducible results, indicating changes in the physical properties of the specimen during the course of the experiments. Such changes are more likely in an impure than a pure specimen.

V. Discussion of Results

(a) *General*

It is evident from an inspection of Figures 2 and 3 that the e.m.f. is not linearly related to stress or temperature or both over the full range in the majority of cases. However, an analysis of the scatter of the observations reveals that the e.m.f. for copper, silver, gold, tungsten, palladium, and platinum may in each case be satisfactorily represented as a linear function of temperature (in the range $T_1=20$ to 100 °C) and of stress (in the range used).

Table 3

Tension coefficient of thermal e.m.f. for $T_1=100$ °C and $T_2=20$ °C

Metal	$\frac{(\Delta E)_{\text{av.}}}{80W}$ (μμV/°C per kg/cm²)	Metal	$\frac{(\Delta E)_{\text{av.}}}{80W}$ (μμV/°C per kg/cm²)
Copper I	$-8\cdot9\pm0\cdot9$	Titanium	-33 ± 7
Copper II*	$-6\cdot7\pm0\cdot5$	Molybdenum	$-0\cdot09\pm0\cdot05$
Silver I	$-13\cdot5\pm0\cdot7$	Tungsten	$-10\cdot0\pm0\cdot5$
Silver II	$-11\cdot4\pm0\cdot4$	Iron I	$-13\cdot5\pm0\cdot5$
Gold I	$-11\cdot8\pm1\cdot5$	Iron II	$-16\cdot3\pm1$
Gold II	$-9\cdot6\pm0\cdot6$	Nickel	-460 ± 15
Gold III	$-7\cdot2\pm1\cdot0$	Palladium	-104 ± 15
Gold IV	$-6\cdot8\pm0\cdot8$	Platinum	-71 ± 2

* The result for copper II has been derived from previous observations (Mortlock 1951) made on commercial wire of unknown purity.

For these metals it is therefore possible to define a single quantity, $(\Delta E)_{\text{av.}}/\{(T_1-T_2)W\}$, describing the behaviour of the material in this region. Such a quantity may be termed the tension coefficient of thermal e.m.f. and evaluated by averaging the difference, ΔE, between adjacent curves at a value of T_1-T_2 equal to 80 °C.

In Table 3 this tension coefficient of thermal e.m.f., as defined above, is given for each of the metals examined; the errors are estimated standard errors.

Although these data suggest that the general effect is dependent upon the purity of the sample, the evidence is not decisive because of the high relative errors. At higher temperatures, however, where the relative errors are smaller, the differences between the tension coefficients evaluated over a common stress range definitely indicate a dependence on purity in each of the four metals so tested.

(b) *Comparison with Other Measurements*

In Table 4 the measurements previously given by Crussard (1948) and Meyer (1896) for non-ferromagnetic metals are compared with the relevant data obtained in the present investigation. It should be noted that this comparison assumes the effect to be a linear function over a wider range of stress than that used by the author, and is thus limited in its significance.

TABLE 4

COMPARISON BETWEEN TENSION COEFFICIENTS OF THERMAL E.M.F. FOUND BY VARIOUS OBSERVERS FOR $T_1 \simeq 100$ °C AND $T_2 \simeq 20$ °C

($\mu\mu$V/°C per kg/cm^2)

Metal	Crussard	Meyer	Author
Copper	—7·1 (mean)	— 6·7	— 7·8 (mean)
Silver	—	—10·1	—12·5 (mean)
Gold	—	— 2·3	— 8·9 (mean)
Aluminium ..	+4	+ 8·1	—
Platinum ..	—	—67	—71

Owing to the large discrepancy between the results for gold, the present measurements were extended to a stress intensity equal to that used by Meyer without, however, producing any great change in the tension coefficient. The discrepancy may be due partly to impurities in Meyer's specimen. The general agreement otherwise is as good as could be expected.

Ferromagnetic metals are a special case which previous experiments (Meyer 1896) have shown to be sensitive to magnetic state. The results given in this paper are only included to show a possible temperature variation of the effect, since no special precautions were taken to ensure the reproducibility of the magnetic state.

(c) *Relationship between Tension and Pressure Measurements*

Assuming small stresses and elastic deformation the change in thermoelectric power $\Delta S_{||}$ parallel to the longitudinal axis of an isotropic polycrystalline wire due to strains $\varepsilon_{||}$ and $\varepsilon_{\perp}$ respectively parallel and perpendicular to the same axis is given by

$$\Delta S_{||}=\beta_{||}\varepsilon_{||}+2\beta_{\perp}\varepsilon_{\perp}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where the β's are a function of temperature only and the ε's are taken to be positive for contraction.

If the strains are brought about by a longitudinal tension t or a hydrostatic pressure p, this equation may be written respectively as

$$\Delta S_{||}=C_t t \quad \text{or} \quad \Delta S_{||}=C_b p, \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

where both t and p are taken as positive and the coefficients C_t and C_p are related to $\beta_{||}$ and $\beta_{\perp}$ by the following equations:

$$\left.\begin{aligned} C_t&=(2\mu\beta_{\perp}-\beta_{||})/Y, \\ C_b&=(2\beta_{\perp}+\beta_{||})(1-2\mu)/Y, \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (3)$$

in which μ and Y are respectively Poisson's ratio and Young's modulus.

Hence if C_t, C_b, and the elastic constants are known for an isotropic metal in a particular state, then the first-order thermoelectric effect of the metal under the same conditions can be calculated for other types of strain.

In experiments of the kind described here $\Delta S_{||}$ is observed directly and is equal to $\partial E/\partial T_1$, T_2 constant. C_t and C_b differ in sign in most cases; this seems to be in agreement with remarks made by Wagner (1908, pp. 996–7), and consistent with the sign of the volume changes, but is at variance with the conclusion reached by Bridgman (1918, p. 376 *et seq.*) and the interpretation of the latter's measurements given in the International Critical Tables (1929).

TABLE 5

THERMAL E.M.F.-STRAIN COEFFICIENTS FOR $T_1 \simeq 100$ °C AND $T_2 \simeq 20$ °C

Metal	$\beta_{\|\|}$ (μV/°C)	$\beta_{\perp}$ (μV/°C)
Gold	11·7	5·6
Silver	14·7	6·2
Copper	10·8	1·3
Platinum	132	13·4
Palladium	125	6·0

Wagner (1908) has made the only large-scale investigation of the effects of pressure at sufficiently low pressures to be combined with the present tension measurements. Use is therefore made of these data, corresponding to a hot junction temperature of about 100 °C, in order to calculate $\beta_{||}$ and $\beta_{\perp}$ for those metals which appear to be linear in this region of stress and temperature. In this calculation the unweighted means for C_t of Table 3 and the elastic constants given by Druyvestein (1946) have been used. Values of $\beta_{||}$ and $\beta_{\perp}$ are shown in Table 5.

(*d*) *Theoretical Consequence of New Result for Gold*

It is of interest to consider how Smit's (1952) conclusions concerning the positions of the Fermi surface for gold, silver, and copper may have to be modified, owing to the very large discrepancy between the present result for gold and that found by Meyer.

The author is indebted to P. G. Klemens* for the following comments on this matter: " Smit calculated $\beta_{||}-\beta_{\perp}$ as a function of the energy gap at the zone boundary (his Fig. 4). To any positive value of $\beta_{||}-\beta_{\perp}$ corresponded

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two values of the energy gap—for one (case (*a*)) the Fermi surface was inside the zone, for the other (case (*b*)) the Fermi surface touched the zone boundary. Requiring that the energy gap should be least for copper and largest for gold, and using the experimental values for $\beta_{\parallel}-\beta_{\perp}$ (0·6 μV/°C for gold, based mainly on Meyer's and Wagner's work), he allocated a position (*a*) for copper, and (*b*) for silver and gold, with large differences in the energy gap. But with the new value of $\beta_{\parallel}-\beta_{\perp}$ (6·1 μV/°C), gold must be moved to a position close to silver, but still case (*b*). This makes it probable that copper also has an energy gap very nearly the same as for silver and gold, and thus may also fit case (*b*)."

VI. Acknowledgments

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