

10 to 100 mA in the bisectrix (y) direction and \vec{H}_0 in the x - y plane, the observed $\Delta V_{x\text{dc}}$ generally shows three sets of oscillations corresponding to all three electron ellipsoids, and is very similar to ΔV_z in the acoustic case. The oscillations are presumably caused by the oscillations in collision time τ associated with the density-of-states oscillations at the Fermi surface. Like the dc current, the "Drude-Zener" part of J_{AEy} interacts with all three electron ellipsoids. Thus, if the "planar" Hall term in E_x were comparable with the MQE term, three sets of oscillations would also be observed in ΔV_x . This is not the case. The data indicate at most a 10% modulation of E_{MQ} by an oscillatory voltage. Because $\Delta V_{z\text{dc}}$ and ΔV_z in the acoustic case are very similar, it appears that the Hall effect of the screening current J_{Sx} is small compared to the Hall effect of the acoustoelectric current J_{AEy} .

In summary, we have verified the existence of the MQE effect by observing the voltage peaks in bismuth. This effect provides another method for the investigation of the geometry of the Fermi surface in solid-state plasmas. Finally, other transverse voltages are observed which arise primarily from Hall effects of the

acoustoelectric current. These effects also provide another method of observing phenomena of the de Haas-van Alphen type in solid-state plasmas.

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¹Y. Sawada, E. Burstein, W. Salaneck, and L. Testardi, preceding paper [Phys. Rev. Letters **18**, 776 (1967)].

²Y. Sawada, E. Burstein, and L. Testardi, J. Phys. Soc. Japan Suppl. **21**, 760 (1966).

³B. Lax, J. Mavroides, H. Zeiger, and J. Keyes, Phys. Rev. Letters **5**, 241 (1960).

⁴G. Smith, L. Hebel, and S. Buchsbaum, Phys. Rev. **129**, 154 (1963).

⁵A rotation of the crystal by $\pm 180^\circ$ about the z axis changes the sign of the off-diagonal components α_{yz} .

⁶T. Yamada, J. Phys. Soc. Japan **20**, 1425 (1965).

⁷For $\vec{q} \parallel \vec{Y}$ and \vec{H}_0 in the x - y plane, the GQA from the hole ellipsoid appears only at higher magnetic field. Because the hole Fermi surface is an ellipsoid of revolution about the z axis, MQE voltages do not appear for holes in this configuration.

⁸R. Parmenter, Phys. Rev. **89**, 990 (1953); and G. Weinreich, T. M. Sanders, Jr., and H. White, Phys. Rev. **114**, 33 (1959).

MELTING-POINT ANOMALIES*

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Some metallic elements have much lower melting points than one would expect from their positions in the periodic system. The metals showing this anomaly are La, Pa, U, and the metals in the first part of the $4f$ and $5f$ series. These elements do not exhibit corresponding anomalies in the cohesive energy, the metallic radius, or other physical properties directly related to the cohesive energy. However, the metals with abnormally low melting points also have much lower values for the shear and Young moduli than would be expected from the number of valence electrons, and it is obviously true that the anomalies in melting point and rigidity can be ascribed to the same basic cause.

Table I gives the observed values for the metallic radius r , and for the melting point M , of metals with empty or completely filled

f shells, while the values of r and M for the $4f$ and $5f$ metals are given in Table II. The quantity v is the number of electrons outside the inert gas core less the number f , of electrons in the f shell.

As discussed elsewhere¹ the metallic radius varies in a very simple manner with v and from period to period. Hence the observed value of r can be used to deduce v for metals for which the v value is not obvious from the chemical properties of the element. The v values assigned to the $4f^2$ and $5f^1$ metals were obtained in this manner.

The numbers given in parentheses in Table I are values of r and M obtained by reasonable horizontal and vertical interpolations.

As seen in Table I the melting point of La is 510° , of Pa 770° , and of U 1300° lower than

Table I. Melting points for elements with empty or filled f shells.

		$3d$		$4d$				$5d-4f$				$6d-5f$	
		r	M	r	M			$f=0$		$f=14$		$f=0$	
		(Å)	(°C)	(Å)	(°C)			r	M	r	M	r	M
								(Å)	(°C)	(Å)	(°C)	(Å)	(°C)
1	K	2.384	64	Rb	2.553	39	Cs	2.744	29			Fr	(2.929) (25)
2	Ca	1.974	838	Sr	2.151	768	Ba	2.239	714	Yb	1.940 824	Ra	(2.402) 700
									920				
3	Sc	1.640	1539	Y	1.800	1509	La	1.876	(1430)	Lu	1.735 1652	Ac	(2.009) (1410)
4	Ti	1.461	1668	Zr	1.603	1852	EkaZr	(1.672)	(1770)	Hf	1.580 2222	Th	1.798 1750
													1560
5	V	1.350	1900	Nb	1.472	2468	EkaNb	(1.535)	(2350)	Ta	1.472 2996	Pa	1.635 (2320)
													1132
6	Cr	1.286	1875	Mo	1.404	2610	EkaMo	(1.464)	(2470)	W	1.412 3410	U	1.568 (2430)

expected from the v value. Table II shows the corresponding anomalies for the $4f$ and $5f$ metals.

The small radii observed for the elements from Yb to W with a filled $4f$ shell, as compared with the observed or interpolated values for the corresponding elements with empty $4f$ shell, demonstrate the "lanthanide contraction" discovered by Goldschmidt.³ This reduction in radius can be attributed to the incomplete screening of the $4f$ electrons. The effective charge of the core is thus greater than indicated by the v value and the metallic radius is correspondingly smaller.

Table II. Melting points for $4f$ and $5f$ metals.

				M	
v	f	r		Obs.	Predict.
		(Å)	(°C)		
$4f$ metals					
Ce	3.2	0.8	1.825	797	1510
Pr	3	2	1.827	935	1460
Nd	3	3	1.822	1024	1480
Pm	(3)	(4)	(1.812)	(1048)	1490
Sm	3	5	1.802	1072	1510
Eu	2.1	6.9	2.052	826	840
Gd	3	7	1.802	1312	1540
Tb	3	8	1.781	1356	1560
Dy	3	9	1.774	1407	1570
Ho	3	10	1.766	1461	1590
Er	3	11	1.757	1497	1600
Tm	3	12	1.747	1545	1620
$5f$ metals					
Np	6	1	1.55	639	2490
Pu	5.3	2.7	1.592	640	2340
Pu ^a	4.8	3.2	1.644		
Am	4.1	4.9	1.730	995	1950
Cm	4	6	1.744	1340	1940

^aValues in the δ forms.

The high melting points observed for the metals Yb-W are probably also due to the incomplete screening of the $4f$ electrons. The reduction in radius Δr , and the increase in melting point ΔM , caused by the screening effect vary with v in a regular manner as seen below.

v	Δr	ΔM
	(Å)	(deg)
2	0.299	110
3	0.141	222
4	0.092	452
5	0.063	646
6	0.052	940

Consider first the $5d-4f$ series of metals. When allowance is made for the increase in melting point due to the $4f$ -screening effect, it is seen that Ba, Eu, and Yb have melting points which are "normal" in relation to their v and r values. Melting-point anomalies occur for the trivalent metals. Because of the screening effect one should have expected a nearly linear increase in melting point from the predicted value of 1430°C for La to the observed value of 1652°C for Lu as illustrated in Fig. 1. All the trivalent metals have melting points (and shear moduli) indicating an effective " v " in respect to melting (and rigidity) which is much lower than the value v associated with chemical properties, metallic radius, or cohesive energy.

As shown in Fig. 2 the melting-point anomalies are even greater for the $6d-5f$ series than they are for the $5d-4f$ group. The effective " v 's" in respect to melting point are listed in Table III.

Since the melting-point anomalies discussed above are restricted to those regions of the periodic system where the $5d-4f$ and $6d-5f$

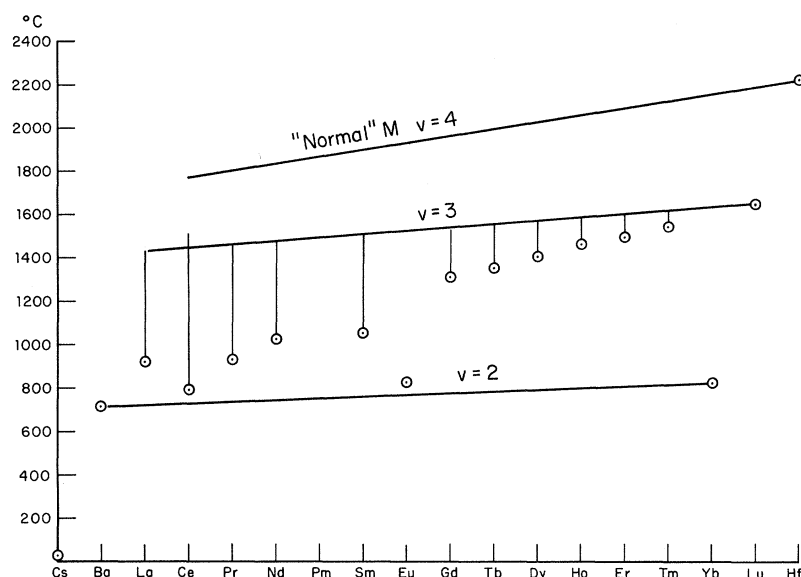


FIG. 1. The observed melting points for the metals Cs to Hf and the predicted "normal" melting points. The magnitudes of the melting-point anomalies are indicated by vertical lines.

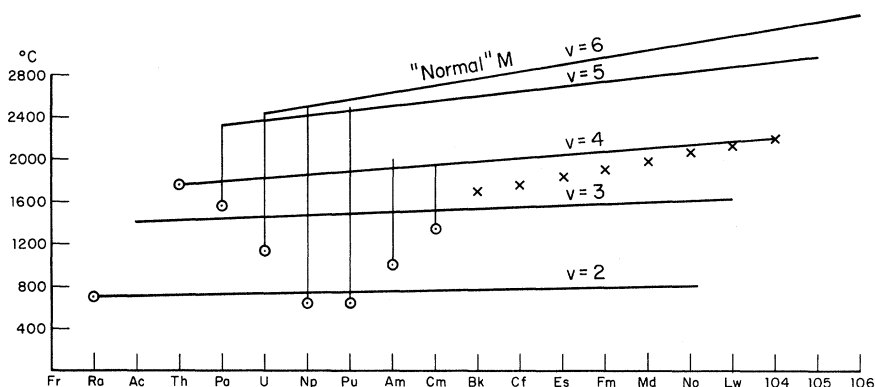


FIG. 2. The observed melting points for the metals Ra to Cm are indicated by circles. (The reported value of 1020°C for Ac is unreasonably low and has therefore been omitted.) The sloping straight lines give predicted "normal" melting points on the assumption that the 5f-screening effect is the same as the 4f-shielding effect. The vertical lines give the magnitudes of the melting-point anomalies.

separations are very small, it is suggested that the basic cause of the anomalies is the presence of some f character in the hybridized wave functions describing the band structure for the valence electrons. It is not unreasonable that a partial f character of the valence band structure will affect melting point and rigidity. However, this interrelationship, which is indicated empirically, has not yet been theoretically established.

Suppose one makes the simplest possible assumption, namely that only the fraction p , of the hybridized wave functions of the valence band having $s-d$ character will affect the melt-

Table III. Effective valence associated with melting point and rigidity.

	v	" v "	$p = "v"/v$		v	" v "	$p = "v"/v$
La	3	2.29	0.76	Er	3	2.69	0.90
Ce	3.2	2.07	0.65	Tm	3	2.81	0.94
Pr	3	2.22	0.74	Lu	3	3	1.00
Nd	3	2.29	0.76	Pa	5	3.4	0.68
Sm	3	2.27	0.76	U	6	2.6	0.43
Gd	3	2.51	0.84	Np	6	1.9	0.32
Tb	3	2.53	0.84	Pu	5.3	1.9	0.36
Dy	3	2.55	0.85	Am	4.1	2.2	0.54
Ho	3	2.63	0.88	Cm	4	2.6	0.65

ing point. On this assumption one has $p = "v"/v$, and one arrives at the p values listed in Table III.

Since $p = 1$ for Ba, Eu, and Th it is implied that there is no contribution from f -wave functions to the band structure of these metals presumably because the d - f separation is too large. According to our hypothesis the metals Yb-W will be normal (except for the $4f$ -screening effect) because the $4f$ level is completely filled. In the series of trivalent metals Ce-Tm the number of vacancies in the $4f$ level decrease from 13.2 at Ce to 2 at Tm and $1-p$ is nearly proportional to the number of vacancies $14-f$, in the $4f$ shell.

As illustrated in Tables I-III and in Fig. 2, the melting-point anomalies are much greater for the $6d$ - $5f$ series than for the $5d$ - $4f$ metals with " v " values as low as 1.9 for Np and Pu. As the $5f$ shell is being filled the anomaly should gradually vanish. The estimated melting points for the transcurium metals shown in Fig. 2 assume that the thoride character of Am and Cm metals persists through the second-half of the $5f$ series.

There is no correlation between melting point and the crystal structure of the metal immediately below the melting point. Thus Y, Ba, La, Ce, Yb, Th, U, and Pa are all body-centered cubic in their high temperature forms, but some have "normal" and other anomalously low melting points. However, at lower temperatures there is a striking correlation between crystal structure and anomalous melting point. The double hexagonal structure of α -La, β -Ce, α -Pr, α -Nd, Am and Cm, and the Sm structure occur only for metals with anomalous melting points. The crystal struc-

tures of Pa, α -U, β -U, α -Np, β -Np, α -Pu, β -Pu, and γ -Pu are all unique. In α -U, α -Np, and α -Pu each metal atom forms four (in α -Pu also three or five) covalent bonds with unusual directions. It is our belief that the strangeness of the low-temperature structures is also due to partial f character of the hybridized wave functions of the valence band.

All the above mentioned elements are strongly magnetic with the exception of La, Pa, and U. These three metals are superconducting, however their transition temperatures do not follow the systematic variation throughout the periodic system.⁴

At present there is not even a satisfactory beginning of a microscopic theory of melting. Speculative discussions, such as given in this paper, are hence justified because they may suggest directions for fruitful theoretical exploration.

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¹W. H. Zachariasen, in *The Law of Mass Action Centenary Volume* (Universitets Forlaget, Oslo, 1964), p. 185.

²L. Pauling, J. Am. Chem. Soc. **69**, 542 (1947).

³V. M. Goldschmidt, T. Barth, and G. Lunde, *Skrifter Norske Videnskaps-Akad. Oslo, I: Mat.-Naturv. Kl.* **1925**, No. 7.

⁴D. C. Hamilton and M. A. Jensen, *Phys. Rev. Letters* **11**, 205 (1963).

CHEMICAL INFLUENCE OF HOLES AND ELECTRONS ON DISLOCATION VELOCITY IN SEMICONDUCTORS

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The velocity of dislocations in semiconductors, as shown in plasticity studies or direct determinations of the dislocation velocity, is strongly affected by the electronic environment of the dislocation in the semiconductor. This is reflected by the following facts:

(i) Donors (such as arsenic) in concentrations

larger than $10^{18}/\text{cm}^3$ raise markedly the dislocation velocity¹ v_D and lower the upper yield stress σ_M and delay or incubation time in creep experiments,² in germanium and in silicon,³ while acceptors (such as gallium) lower markedly v_D and raise σ_M . Neutral impurities in the same concentration range have no effect