The Magnetic Properties of Liquid Ge-Te Alloys

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The magnetic behaviour of the liquid system Ge–Te has been determined with the help of susceptibility measurements. Two pronounced minima have been observed indicating the persistence of locally ordered regions in the liquid state. The minimum at the equiatomic composition, although markedly decreasing with increasing temperature, persists up to at least 1330 K. The second minimum located at the eutectic composition (85 at %Te) was found to be extremely temperature dependent and disappeared within 100 K above the eutectic temperature. A theoretical treatment has been attempted within the framework of the free electron approximation.

(Die magnetischen Eigenschaften flüssiger Ge–Te Legierungen)

Das magnetische Verhalten des flüssigen Systems Ge–Te wurde anhand von Suszeptibilitäts-messungen bestimmt. Es wurden zwei ausgeprägte Minima festgestellt, welche auf das Vorliegen von lokal geordneten Bereichen im flüssigen Zustand schließen lassen. Obwohl das bei 50 At %Te vorhandene Minimum mit zunehmender Temperatur merklich abnahm, blieb es zumindest bis 1330 K erhalten. Das zweite bei der eutektischen Zusammensetzung befindliche Minimum (85 At %Te) erwies sich als ausnehmend temperaturabhängig und verschwand innerhalb 100 K oberhalb der eutektischen Temperatur. Eine theoretische Behandlung wurde mittels des Modells freier Elektronen versucht.

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INTRODUCTION

The transport properties of liquid tellurium and their variation with temperature have always been assigned to the local structure of the melt and its evolution as function of temperature. The results of numerous investigations concentrated on the structural changes of liquid tellurium cast strong doubts on the concept of tellurium chains in the liquid state. In contrast to Se, where a chain-like structure is retained in the liquid state giving rise to semiconducting properties, a more metallic behaviour of liquid Te seems to be indicated by the electrical conductivity,[1,2] Hall coefficient,[3-6] Knight shift[7-9] and magnetic susceptibility.[19-11] Instead of a twofold coordinated chain-like structure, which might indeed be stable in the supercooled region, Cabane and Friedel[8] proposed a structure consisting of sites with two and three covalent bonds in coexistence with a metallic-like electron gas. In fact, the nearest neighbour coordination deduced by Tourand and co-workers[12-14] from neutron diffraction experiments is clearly higher than that of a chain-like structure and tends to increase drastically with the temperature. Very recent Raman scattering experiments also indicated a non-chain-like short range order in liquid Te.[15] Despite the strong evidence against a chain-like structure in the stable liquid state and even 50 K below the melting point (723 K), the formation of short chains at least in extremely supercooled Te could not definitely be excluded.[14] The obvious structural peculiarities of liquid Te have stimulated numerous authors to study the properties of Te-based alloys. Among the many liquid Te-alloys studied so far, special attention has been paid to systems with a Te-rich eutectic, such as Tl–Te, In–Te, or Ge–Te. The thermodynamic investigation of the Ge–Te system reported by Glasov and Pavlova[16] yielded deep minima of the enthalpy and the entropy of mixing which have been assigned to the formation of GeTe and $GeTe_2$ associations. DeNeufville discussed the glass forming ability of liquid Ge–Te on the basis of the structural peculiarities in the range of $GeTe_2$.[17] In an earlier paper Bergman and Castanet showed that the heat capacity of liquid GeTe increased considerably on approaching the congruent melting point suggesting the preformation of a local order similar to that of crystalline β-GeTe.[18] Valiant and Faber reported a flat maximum of the electrical resistivity and the thermoelectric power at about 67 at %Te.[19] The very careful magnetic measurements by Takeda and Tsuchiya revealed a minimum of the magnetic susceptibility near the equiatomic composition pointing to the existence of local order.[20] In a very recent work focused on the heat capacity at the eutectic composition Castanet and Bergman observed a very marked deviation from additivity and an extremely high temperature coefficient near the eutectic temperature.[21] In view of the very striking results it seemed to be worthwhile to

repeat the magnetic measurements with special emphasis on the eutectic composition.

EXPERIMENTAL

High purity tellurium lumps (99.999 %, Asarco, New York, USA) and semiconductor grade germanium bars (Alfa, Mass., USA) have been used as starting materials. Appropriate amounts of the elements were placed in quartz ampoules especially designed for the magnetic measurements, evacuated, and flushed repeatedly with purified argon, and ultimately sealed under vacuum (0.01 Pa). During the sealing procedure the samples were cooled to minimize the error introduced by the loss of tellurium. The mixtures were slowly heated up to 1300 K, kept there for about two hours, and then cooled again to room temperature at a rate of 1 K min^{-1}. The magnetic measurements were performed on a Faraday-type magnetic balance designed by Beisswenger and Wachtel.[22] The magnetic suscepti-bilities were recorded both on heating and cooling in the range from room temperature up to about 1300 K at a rate of 5 K min^{-1}. The contribution of each individual quartz ampoule to the magnetic susceptibility, hardly accessible by direct measurement due to experimental difficulties, was assumed to be proportional to its mass. This could be verified by measuring a series of empty ampoules differing in size and mass. All in all, the maximum error of the reported susceptibility was estimated to be of the order of $\pm 4.10^{-11}$ m^3 mol^{-1}.

RESULTS AND DISCUSSION

In accordance with earlier investigations[11,23] we observed that on melting pure Ge changes from a diamagnetic solid to a paramagnetic liquid (Figure 1). The change of sign reflects the competition between the diamag-netism of the core atoms χ_{dia} and the paramagnetic contribution of the conduction electrons χ_e which is proportional to the density of states at the Fermi energy. In the free electron approximation the total magnetic susceptibility can be expressed by

$$\chi = \chi_{dia}(Bz^+) + \alpha \cdot \frac{3\mu_0 \mu_B^2 m_e N_A^{1/3}}{\hbar^2(3\pi)^{2/3}} \cdot z^{1/3} \cdot V_A^{2/3} \qquad (1)$$

V_A is the molar volume, z the number of valence electrons transferred to the conduction band, α is the exchange enhancement factor which is $\frac{2}{3}$ in the case of free non-interacting electrons. N_A, m_e, μ_B, μ_0, and $\hbar$ have their usual
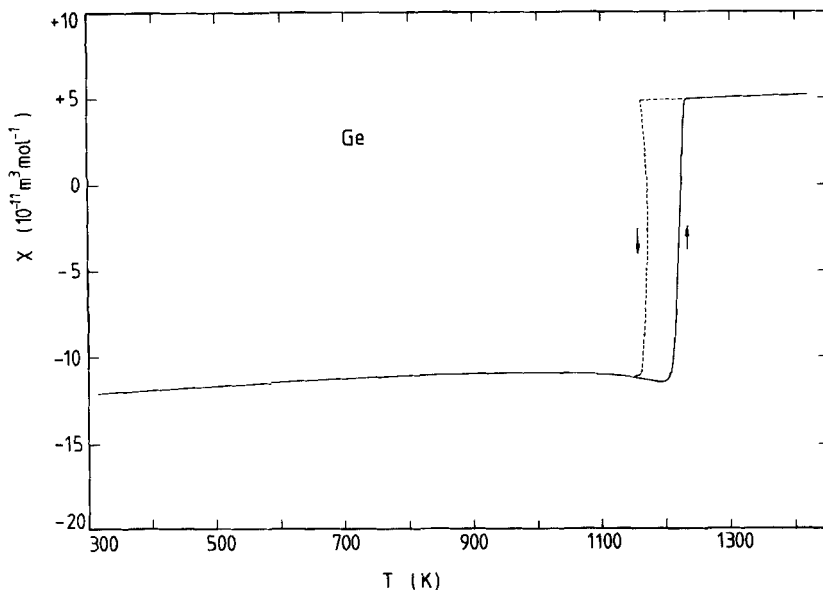
FIGURE 1   Magnetic susceptibility of Ge as function of temperature.

meanings. Hall effect measurements[5] on liquid Ge indicated the presence of about four conduction electrons per atom ($z = 4$), in good agreement with the result deduced from optical measurements.[24] Applying Eq. (1) to liquid Ge at the melting point ($\alpha = \frac{2}{3}$, $z = 4$, $\rho = 5.49$ g cm^{-3} [25] and using the diamagnetic values given in the literature[26,27] for Ge^{4+} (-8.8 or $-10.3 \cdot 10^{-11}$ m^3 mol^{-1}) we would expect a total susceptibility of 5.1 or $3.6 \cdot 10^{-11}$ m^3 mol^{-1} which is indeed within the experimental accuracy identical to our experimental value of $5 \cdot 10^{-11}$ m^3 mol^{-1}.

For the further treatment we considered our experimental value to be correct and assumed χ_{dia} to be $-8.9 \cdot 10^{-11}$ m^3 mol^{-1} so as to satisfy Eq. (1). The weak temperature dependence of the magnetic susceptibility is determined by the variation of the molar volume with the temperature, again in good agreement with the free electron model.

The marked temperature dependence of the magnetic susceptibility in liquid Te, extremely pronounced in the supercooled range where the discontinuity on crystallization is reduced by a factor of two, is certainly not due to the variation of V_A (Figure 2). Following the arguments of Cabane and Friedel[8] the number of free electrons seems to be coupled to the local structure of liquid Te which in turn varies with temperature. Consequently, we have to expect a variable number of electrons, in contrast to liquid Ge where a constant number of free electrons is indicated. The unusual tem-
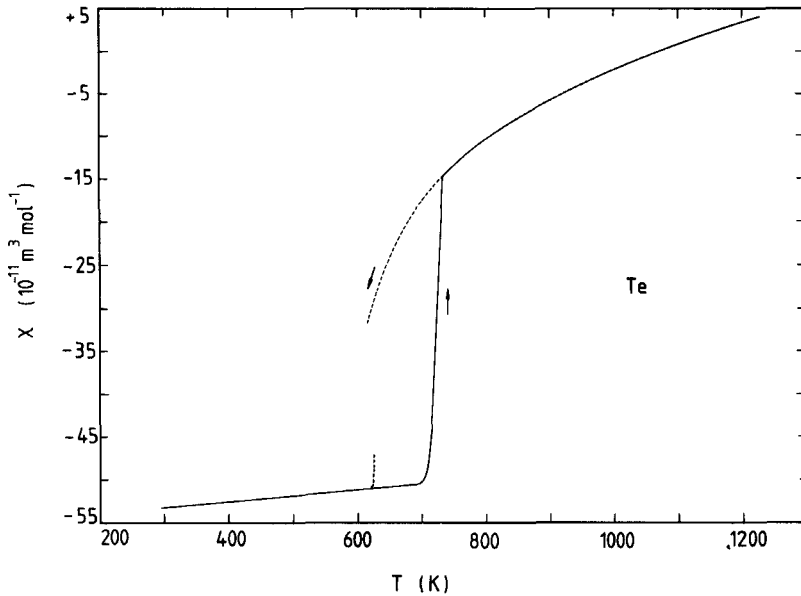
FIGURE 2 Magnetic susceptibility of Te as function of temperature.

perature dependence of the susceptibility undoubtedly reflects the changes in the structure of liquid Te. The Knight shift which is expected to be proportional to the electronic paramagnetism showed also a very strong temperature dependence.[7–9] It has been reported that the diffusion coefficient in liquid Te decreases rapidly near the melting point[28] and the heat capacity tends to increase on cooling.[29] Based on extensive neutron diffraction studies Tourand and coworkers[12–14] concluded that the number of first nearest neighbours increases at the expense of the second nearest coordination shell from 3 at the melting point up to about 6 at 2200 K. Cabane and Friedel assumed a three dimensional network of sites with twofold and threefold coordination, the latter being dominant at elevated temperatures.[8] Recent Raman scattering experiments near the melting point confirm the three-dimensional local structure proposed by Cabane and Friedel and cast doubt on the formation of Te-chains, at least in the stable liquid state.[15] Even in supercooled Te the coordination number turned out to be considerably larger than two, as one would expect for a chain-like structure.[14]

In this paper the enhancement factor α was determined with the help of the Hall coefficient. Figure 3 shows the number of conduction electrons z deduced from the Hall coefficient R by using the free electron expression $z.e.R = -V_A/N_A$ as function of temperature. The data have been taken from the papers of Busch and Tieche[5] ($\square$), Tieche and Zareba[3] ($\bigcirc$), and Enderby
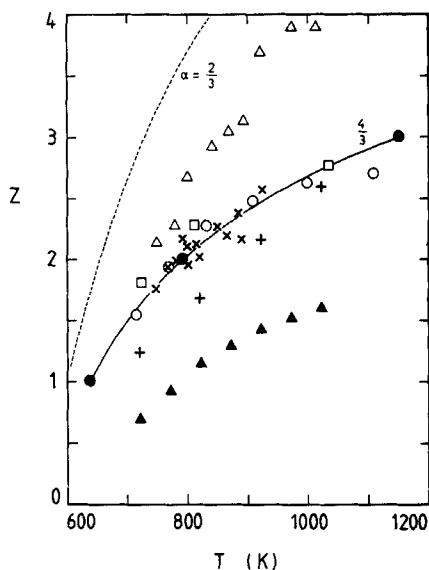
FIGURE 3   Number of free electrons deduced from the magnetic susceptibility ($\bullet$), Hall coefficient [3-6] (O, $\times$, $\square$, $\triangle$), Knight shift[8] ($+$), and density of states[6] ($\blacktriangle$).

and Walsh[4] ($\times$). The values given by Cabane and Friedel[8] are based on Knight shift data ($+$). The results given by Okada et al.[6] have also been used ($\triangle$), however, the authors preferred a different interpretation. We also used their density of states data to estimate the number of free electrons on the basis of a free electron behaviour ($\blacktriangle$). Our own values ($\bullet$) were obtained by applying Eq. (1) and considering the temperature as implicit parameter. The molar volumes were based on the data given by Lucas and Urbain.[30] The diamagnetic susceptibilities of the cores were taken directly from the literature or estimated by interpolation of the existing data.[26,27,31,32] We obtained values (-51.1, -41.8 and $-34.7.10^{-11}$ m^3 mol^{-1} for Te$^+$, Te^{2+} and Te^{3+}) which are not too far from those derived from the liquid systems Se–Te,[6] Tl–Te[33] and Ag–Te[34] (-44.6, -52.8 and $-45.9.10^{-11}$ m^3 mol^{-1}). Based on the Knight shift in pure liquid Te Warren[9] deduced a value of $-56.5.10^{-11}$ m^3 mol^{-1}. Dissimilar to the constant values quoted above, we considered the diamagnetic contribution to be a function of temperature. The best fit to the Hall effect based data was achieved with $\alpha = \frac{4}{3}$. Cabane and Friedel[8] have assumed an enhancement factor of 1.5, Okada et al.[34] reported a value higher than 2, similar to that estimated by Warren.[9] It must be admitted that our value of $\frac{4}{3}$ has certainly some arbitrary character, since we always used the free electron expressions which might be a simplification of the problem. In fact, the positive thermoelectric power observed in liquid

Te is not compatible with this simple model which predicts a negative sign of the Seebeck coefficient.[35,36] Since this paper is not primarily aimed at a profound theoretical treatment of the transport properties in liquid Te, we abstained from using the more elaborate concept of Friedman[37] which accounts for this sign discrepancy.

The phase transformations which are expected to occur according to the Ge–Te phase diagram are indicated by more or less pronounced discontinuities of the magnetic susceptibility as shown in Figure 4 for three different
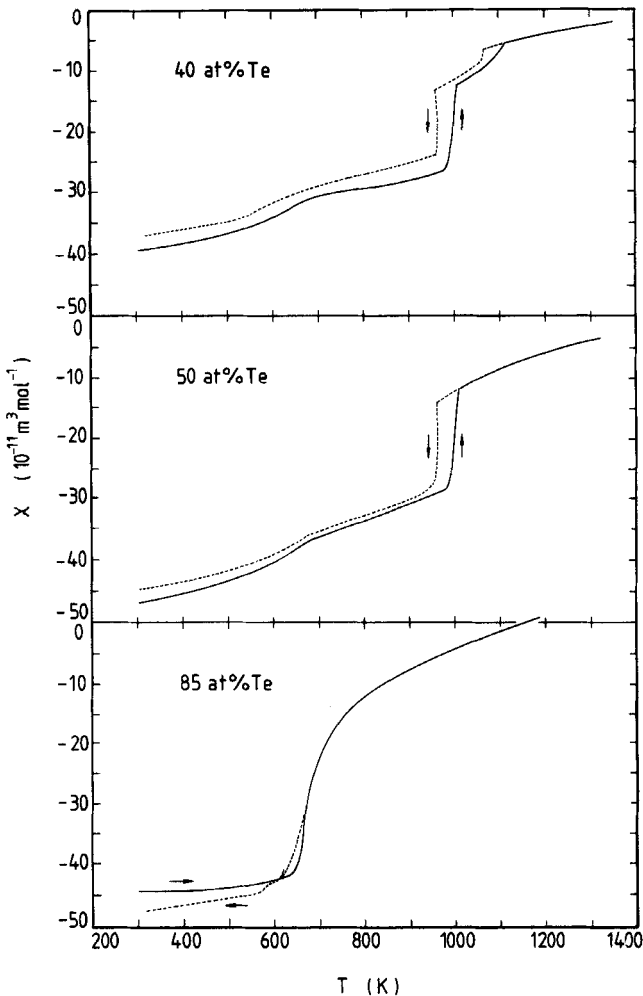

FIGURE 4   Magnetic susceptibility of Ge–Te alloys as function of temperature.

compositions (40, 50 and 85 at %Te). The improved phase diagram reported by Legendre and Souleau[38] shows three different phases near the equiatomic composition: rhombohedral α-GeTe, B1-type β-GeTe (high temperature form of α-GeTe), and orthorhombic γ-GeTe. The change of slope at about 680 K in Ge-rich alloys (40 and 50 at %Te) is certainly due to the peritectoid reaction $\alpha \rightleftharpoons Ge + \beta$. The sharp discontinuities around 1000 K reflect the eutectic reaction $\beta + Ge \rightleftharpoons L$ (40 at %Te) and the congruent melting of the β-phase (50 at %Te), respectively. The break at 1120 K denotes the liquidus temperature at 40 at %Te. It is very striking that the drastic increase of the susceptibility on melting, the most pronounced effect throughout the phase diagram, was not apparent at the Te-rich eutectic at 85 at %Te. In contrast to all other compositions, the change from the solid to the liquid state seems to be accompanied by a rapid but smooth variation of the magnetic suscepti-
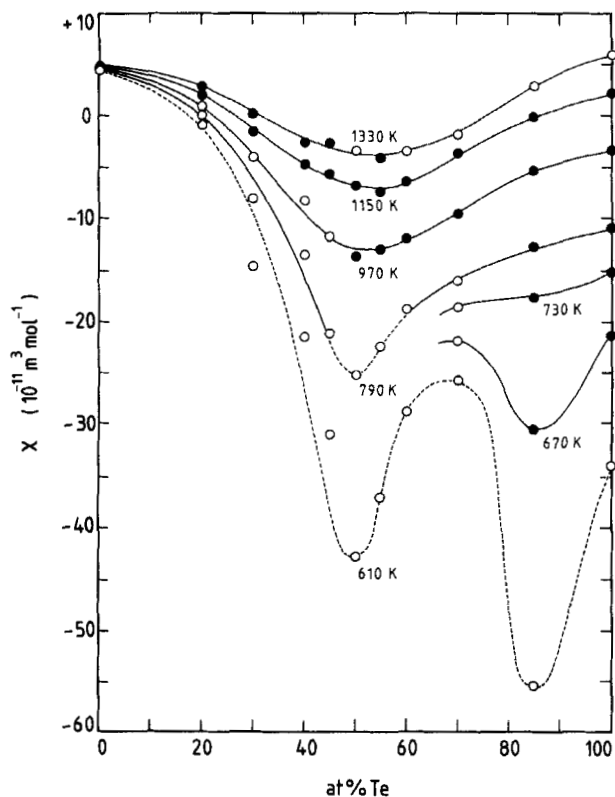

FIGURE 5   Magnetic susceptibility of liquid Ge–Te alloys as function of temperature and composition.
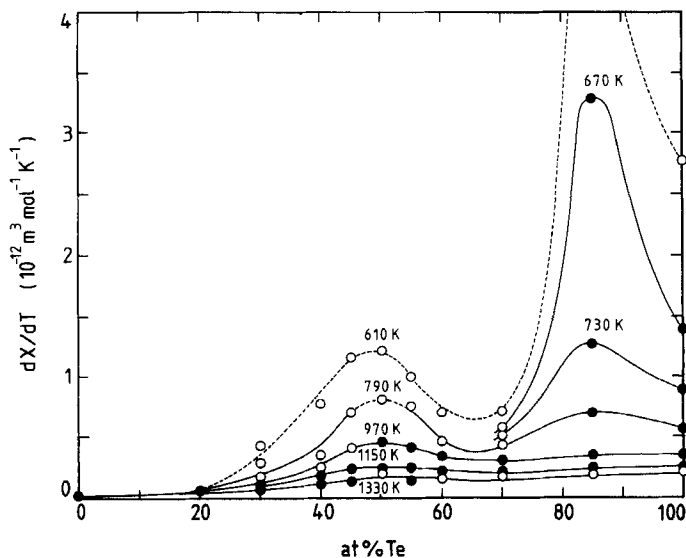
FIGURE 6   Temperature coefficient of the magnetic susceptibility of liquid Ge–Te alloys as function of temperature and composition.

bility. It is unclear, whether the small discontinuity and the hump observed on cooling around 600 K can be assigned to the eutectic reaction $L \rightleftharpoons \alpha$ + Te and the peritectoid formation of γ-GeTe according to α + Te $\rightleftharpoons \gamma$. Parthasarathy et al.[39] have illustrated the complexity of the crystallization process in the glass forming region between 78 and 87 at %Te. Comparing our temperatures with those given in literature, we observed that the peritectoid reaction $\alpha \rightleftharpoons$ Ge + β occurs 20 K below the temperature given by Legendre and Souleau.[38] In addition we found the liquidus on the Ge-rich side considerably lower than given by Hansen and Anderko;[40] this has already been pointed out by Bergman and Castanet.[41] Furthermore we concluded that the magnetic susceptibility of the crystalline phases increased successively from α to γ.

The isothermal representation of the magnetic behaviour of the liquid system Ge–Te is shown in Figure 5 for 610, 790, 970, 1150 and 1330 K. On account of the nonlinearity of the χ vs. T curves the extrapolated values (O) are certainly not very reliable, particularly in the range between 40 and 60 at %Te where an accuracy not better than $\pm 20\%$ has to be expected. The dotted line given for the lowest isotherm (610 K) indicates the very high degree of uncertainty. Despite the lack of accuracy discussed above the essential features — two deep minima at 50 and 85 at %Te, respectively — are clearly apparent. The minimum located at about 50 at %Te is less pronounced

but stable also at high temperatures, while that observed at 85 at %Te disappeared dramatically within 100 K above the eutectic temperature (640 K). This is more explicitly expressed by the temperature coefficient of the magnetic susceptibility which identifies two regions of maximal temperature dependence (Figure 6).

Our observations are in excellent agreement with the heat capacity measurement reported by Castanet and Bergman.[18,21] Their results show that at 50 at %Te the excess heat capacity is positive and disappears at about 450 K above the melting temperature pointing to the existence of heteroclusters in the range above the melting point. So far we are also tempted to speculate with some kind of local order or association in the liquid state which could be responsible for the minimum of the magnetic susceptibility around 50 at %Te. Similar conclusions have been drawn by Takeda and Tsuchiya[20] who also observed a minimum of the magnetic susceptibility at about 45 at %Te and a rather flat maximum of the temperature coefficient near 50 at %Te. Their data refer to the high temperature range from 1170 to 1320 K where we also observed only one minimum of the susceptibility at 55 at %Te and one flat maximum of the temperature coefficient at about 50 at %Te. The unique behaviour at 85 at %Te has obviously not been observed which is probably due to its exclusive appearance within a restricted range near the eutectic point. The recent investigation of Castanet and Bergman[21] confirms the striking behaviour at the Te-rich eutectic. They report unusually high values of the excess heat capacity decreasing from 183 J mol^{-1} K^{-1} at 650 K to zero at 790 K indicating a second order transformation near the eutectic temperature. Similar data are reported by deNeufville who discussed the results in terms of chemical bonding and ordering.[17] Unlike the case of pure liquid Te, where the heat capacity increases only slightly on approaching the melting point,[29] we are inclined to speculate with the existence of short Te-chains near the eutectic temperature. Despite the strong experimental evidence against a chainlike structure in liquid Te we may ask the question whether the dramatic increase of the heat capacity near the eutectic point is caused by the formation of short chains or some other type of short range order. A further discussion on the details of the liquid structure goes beyond the scope of this paper. Due to the lack of own thermodynamic data we are unable to include the possibility of GeTe and GeTe$_2$ associations proposed by Glasov and Pavlova[16] into our discussion.

From the magnitude of the electronic susceptibility, obtained by subtracting the diamagnetic core contributions of Ge^{4+} and Te^{4+} from the experimentally observed value, Takeda and Tsuchiya concluded that the electronic state of liquid GeTe is far from being localized.[20] According to our view the diamagnetic cores of Te vary formally from Te$^+$ at 640 K to
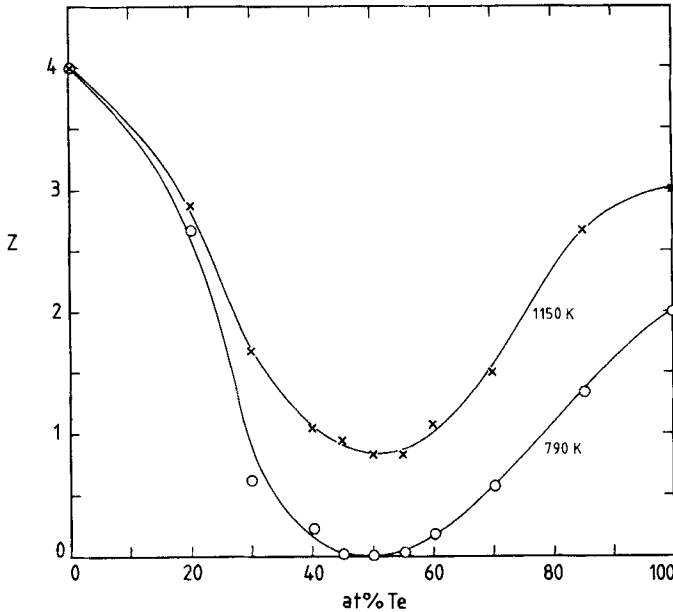
FIGURE 7   Number of free electrons in liquid Ge–Te alloys as function of temperature and composition.

Te^{3+} at 1150 K, therefore we considered it necessary to redetermine the degree of localization by applying the free electron approximation used in this paper. As first approximation we assumed both the enhancement factor α and the density varying linearly between the values of the pure elements. By using Eq. (1) we obtained the results shown in Figure 7 for two different temperatures. As compared to the additive values expected for the equiatomic composition (3 at 790 K and 3.5 at 1150 K) our calculations yielded a considerably reduced number of free electrons per atom implying a high degree of localization. In fact, Glasov et al.[42] reported a clear maximum of the electrical resistivity at about 55 at %Te, whereas Valiant and Faber observed only a flat maximum located around 67 at %Te.[19] Concerning the significance of the parameters deduced in this paper we have to emphasize the tentative character of our theoretical treatment. Additional measurements focused on the structural peculiarities of liquid Ge–Te are required to substantiate the conclusions drawn so far.

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