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PHYSICAL REVIEW B VOLUME 8, NUMBER 4 15 AUGUST 1973

Magnetic Susceptibility of the Noble Metals around Their Melting Points

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The magnetic susceptibilities of the noble metals have been accurately measured close to the melting point in both liquid and solid states. In the liquid the susceptibilities are (in cgs volume units) Cu: $(-0.70\pm0.01)\times10^{-6}$, Ag:$(-2.05\pm0.01)\times10^{-6}$, Au: $(-2.74\pm0.01)\times10^{-6}$, and in the solid Cu: $(-0.59\pm0.01)\times10^{-6}$, Ag: $(-1.84\pm0.01)\times10^{-6}$, Au:$(-2.63\pm0.01)\times10^{-6}$. The results obtained agree well with the susceptibilities calculated recently by Borchi and de Gennaro if the effects of electron-electron interactions are correctly taken into acount.

There is considerable uncertainty in the experimental values for the magnetic susceptibility of the liquid noble metals.[1] For instance, different authors obtain opposite sign changes in the susceptibility for copper on melting. Knowledge of the spin susceptibility is important in the interpretation of the Knight shifts in these metals.[2,3] Furthermore, Borchi and de Gennaro[4] have recently calculated the electronic susceptibility of the noble metals in both liquid and solid state using a pseudopotential method. They predict that, even in the liquid, there are considerable deviations from free-electron behavior with the paramagnetic term being enhanced and the diamagnetic term reduced. We have therefore made measurements by the Faraday method of the magnetic susceptibility of high-purity (99.999% or better) copper, silver, and gold through their melting points. The values obtained were highly reproducible and the samples showed no sign of oxidation or contamination.[5] The results are given in row 5 of Table I for the liquid metals and in row 9 for the solid metals. The values for the liquid-metal susceptibility are all more paramagnetic and the changes on melting smaller than the mean of the earlier measurements.[1] The value for copper agrees with a recent measurement of Collings[6] and that for silver is within the spread of earlier measurements. The only previous measurement for gold[7] was made rather long ago. Our values are compared with those deduced theoretically in Table I. The effect of the ions on the noninteracting electronic susceptibility has been taken from Borchi and de Gennaro,[4] who took into account the effects of electron-electron (ee) interactions on the spin susceptibility χ_p, using the calculation of Silverstein.[8] However, recent calculations[9,10] have shown that Silverstein seriously underestimated this effect on χ_p and we have therefore used the results of these calculations to obtain a theoretical estimate of χ_p [i.e., $\chi_p=\chi_p^{\text{free}}\,(1+\Delta_p)\,(\chi_{pee}/\chi_p^{\text{free}})$, where Δ_p takes into account the effect of the ions and $\chi_{pee}/\chi_p^{\text{free}}$ is the ratio of the susceptibility including ee interactions to the noninteracting susceptibility.] The effects of ee interactions on the diamagnetic susceptibility have been included using the calculation of Kanazawa and Matsudawa,[11] although the change in the total electronic susceptibility due to this is small (less than 4% in all cases). The theoretical electronic susceptibility χ_e is given in row 3 for the liquid metals and row 7 for the solid metals, and the free noninteracting value χ_{e0} is given for comparison in row 2. It can be seen that the effect of interactions is considerable. The ion-core values χ_i (row 1 and 6 of the table) are those used in Ref. 1, where it was shown that values calculated using modern free-atom wave functions did not give consistent χ_e values for most metals. The total theoretical susceptibilities are given for the liquid in row 4 and in row 8 for the solid metals. For silver the agreement between theory and experiment is very good in both liquid and solid states and the agreement is also very good for solid copper, although the theoretical change in melting is a bit too large. For gold the apparent agreement is poor; however, the ion-core susceptibility of gold is the largest of any metal and any error in this will dominate the susceptibility. If

TABLE I. Susceptibility in 10^{-6} cgs volume units of the noble metals. χ_i is the ion-core susceptibility, χ_e is the electronic susceptibility, and χ_{e0} the noninteracting free-electron susceptibility.

	Cu	Ag	Au
		Liquid	
χ_i	−2.44	−3.60	−5.10(−4.26)
χ_{e0}	0.63	0.55	0.55
χ_e	1.45	1.45	1.52
$\chi_{\text{theor.}}$	−0.99	−2.15	−3.58
$\chi_{\text{expt.}}$	−0.70 ± 0.01	−2.05 ± 0.01	−2.74 ± 0.01
		Solid	
χ_i	−2.54	−3.74	−5.37(−4.49)
χ_e[a]	1.99	1.86	1.85
$\chi_{\text{theor.}}$	−0.55	−1.88	−3.52(−2.64)
$\chi_{\text{expt.}}$	−0.59 ± 0.01	−1.84 ± 0.01	−2.63 ± 0.01

[a] The theoretical electronic susceptibility in the solid is practically identical for both the pseudopotential form factors used by Bochi and de Gennaro.

the ion-core susceptibility for gold is correct, then the electronic susceptibility would be ~50% greater than the already considerably enhanced value in row 3, which seems unlikely. (The Hartree-Fock free-atom value for χ_i would give a value for χ_e smaller than the free noninteracting value, which is also very unlikely.) The ion-core susceptibility for gold which would give agreement for the liquid-metal susceptibility is given in brackets in row 1. Rows 6 and 9 give the susceptibilities in the solid metal consistent with this value of χ_i in the liquid. Clearly, such a procedure gives excellent agreement with experiment for the change on melting. This is unlikely to be fortuitous because of the change in electronic susceptibility (rows 3 and 7) upon melting.

The calculation of Borchi and de Gennaro uses a pseudopotential obtained from low-temperature measurements so that, strictly, the calculation of the effects of the ions on the electronic susceptibility is valid at low temperatures; however, for silver and gold the measured mass susceptibility is practically independent of temperature between 300 K and the melting point, indicating that changes in the electronic susceptibility with volume are small. For copper the susceptibility is quite strongly temperature dependent, becoming more paramagnetic at high temperatures. (The room-temperature susceptibility is, in agreement with earlier workers, -0.77×10^{-6} cgs volume units.) This temperature dependence is approximately twice that expected from volume changes alone, so that χ_e must increase as the temperature increases. The measured change is consistent with an increase of about 3% in χ_p from room temperature to the melting point. The present results may also be compared with the NMR measurements for copper of El-Hanany and Zamir. They attribute the observed temperature dependence of the Korringa product enhancement to the effect of the volume coefficient of m^* on the ee interaction parameter α. In this way they obtain a self-consistent explanation of the behavior of the Knight shift K, and spin-lattice relaxation time, but their deduction of a value of m^* which decreases with increasing temperature is difficult to reconcile with the measured susceptibility changes. As an alternative one can obtain a consistent interpretation of χ and K in which the room-temperature Knight shift (0.237%) comes from our deduced χ_p of 2.1×10^{-6} cgs volume units together with an electron density of the nucleus, P_F, of 1.7 a.u., which is the value calculated recently by Misetich, Hodges, and Watson.[12] The 5% increase in K from room temperature to the melting point is attributable to roughly equal increases in χ_p and P_F, and the change in K on melting (+4%) to a decrease in χ_p of ~10% and an increase in P_F of 10–15%. Naturally, this leaves the behavior of the Korringa product unexplained.

In view of the over-all agreement between the theoretical and experimental susceptibilities given in the table we believe that the calculation of Borchi and de Gennaro gives a good representation of the effect of the ions on the electronic susceptibility of the noble metals. Whilst the static properties, susceptibility, and Knight shift may be consistently interpreted it is not yet possible to include the spin-lattice relaxation, which depends upon the dynamic susceptibility, in such an explanation.

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PHYSICAL REVIEW B VOLUME 8, NUMBER 4 15 AUGUST 1973

Symmetry-Forbidden Resonant Raman Scattering in Cu_2O

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We have observed resonant Raman scattering from the two longitudinal branches of the Raman-forbidden F_{1u} modes of Cu_2O. The agreement between our measured scattering cross section as a function of excitation frequency and a calculated cross section which assumes an intraband Fröhlich electron-phonon interaction is good. This represents a quantitative confirmation of the resonant-Raman-scattering theory proposed by Martin.

There has been considerable interest in the recent literature in the breakdown of selection rules observed in Raman scattering when the frequency of the laser is nearly resonant with an electronic energy level of a crystal.[1–8] With the exception of some work reported by Anastassakis and Burstein,[4] on II-IV semiconductor compounds, the only experimentally observed breakdowns have been relatively minor, consisting of anomalously strong multiple-phonon lines,[6] or the appearance of Raman-allowed LO phonon lines in a forbidden polarization configuration.[5–7]

On the basis of such a breakdown observed in CdS, Martin examined the implications of an assumed intraband Fröhlich electron-phonon interaction and proposed it as an explanation for the polarization anomaly in CdS.[1] Unfortunately, later work showed that with 4880-Å excitation, even in more nearly perfect crystals than Martin and Damen used,[7] defect-related electronic states (bound excitons) dominate in the scattering.[5,9] These defect-related states do not experience translational symmetry, so that *k* conservation is not required. The lack of *k* conservation is quite sufficient to explain the "breakdown."[10] Martin's intraband Fröhlich interaction probably is operative in this case, but it is not required to explain the breakdown.

We report here experimental observation of the two Raman-forbidden LO phonons in Cu_2O when the laser is near resonance. Such a major breakdown of selection rules in crystals with inversion symmetry was predicted by Martin,[1] and has been observed previously in some of the II-IV semiconductors.[4] Cu_2O has been more extensively studied than the II-IV semiconductors, however, and for this reason, meaningful basic calculations of the variation of the Raman scattering efficiency become possible for Cu_2O. Comparison of the results of this calculation with the experimental data allows a meaningful test of the intraband Fröhlich mechanism and of the assumed importance of excitonic states in the resonance. We have performed such a calculation, and the results are reported here. The details of the calculation and of the experiment will be presented elsewhere. With the possible exception of the work of Gross *et al.*[8] these results form the basis of perhaps the first real test of Martin's breakdown mechanism, and of the relative importance of the free excitonic states in the resonance.

Cu_2O has the cuprite structure, space group O_h^4, with two molecules per unit cell. The usual symmetry considerations predict the following zone-center phonon modes: two infrared-active F_{1u} modes, one Raman-active F_{2g} mode, and an A_{1u}, an E_u, and an F_{2u} mode, all silent in both infrared and Raman spectra. Since the crystal has inversion symmetry, the infrared-allowed modes are Raman forbidden and vice versa.

Infrared-absorption experiments have placed the LO phonons belonging to the F_{1u} representation at 645 cm^{-1} and at 149 cm^{-1}. The TO associated with the upper LO is at 611 cm^{-1}, and the lower TO is at 146 cm^{-1}.[11] Balkanski *et al.* have attributed a feature seen in the Raman spectrum at 220 cm^{-1} to the Raman-active phonon.[12] We observe a similar feature in the Raman spectrum at 220 cm^{-1}, but we do not observe the correct polarization character for that feature.[13]

The spectra we report here were taken using a standard Raman scattering setup. The scattering geometry was similar to that of Balkanski *et al.*,[12] except that the polarization of the laser was always parallel to the sample face. The sample was cooled using an Air Products Cryotip cryostat. The sample surface was chemically polished, since mechan-